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(54) A METHOD FOR THE POLYMERISATION OF MONOMERS AND CROSSLINKING OF POLYMERS

(71) We, UNION CARBIDE CORPORATION, a Corporation organised under the laws of the State of New York, United States of America, of 270 Park Avenue, New York, State of New York. 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of cross-linked polymers. More particularly it pertains to the use of an artificial source of predominantly continuum visible light radiation with a radiance of at least about 350 watts per square centimeter steradian for polymerizing monomers to produce crosslinked polymers and for curing or crosslinking preformed polymers and polymer-containing compositions; and to the finished articles produced therewith.

The use of electron beam radiation generated with a nuclear reactor, Van de Graaff accelerator, linear accelerator, radioactive elements such as cobalt 60 or strontium 90, and the use of ultraviolet light generated with a mercury lamp for the polymerization of monomers and the crosslinking or curing of polymers is well known. It is also known that the reactions can be carried out with the presence of free radical initiators in the

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reactants, or with the presence of photosensitizers or crosslinkers. This knowledge is common knowledge to those of ordinary, average skill in the art and will not be repeated here since it can be found in a multitude of published texts, technical journals and patents.

The use of radioactive materials and electron beam accelerators, while efficient, suffers many deficiencies. Chief of these are the high construction costs involved to protect the surrounding areas from the radioactive emissions and the expensive precautions that must be taken to insure that the workers do not become overexposed. Further, in many instances this form of radiation has a degradative effect on the material being treated, for example, cellulosic materials; also, electron beam radiation is not as efficient since most of the high energy electrons pass through the coating film and are absorbed by the substrate rather than being fully utilized to cure the film.

The use of low to medium pressure mercury lamps to generate ultraviolet light is a known alternative. However, the lifetime of such mercury lamps and the costs of replacement detract from their practicality. The largest such mercury lamp of commercial utility is generally about five feet long having an electrical input of about 20 milowatts and an average lifetime of about 2,000 hours. On failure the entire mercury lamp must be replaced, an expensive procedure requiring a maintenance crew. Smaller low to medium pressure mercury lamps also have relatively short life spans and upon failure must be completely replaced. Among the deficiencies and problems faced by the use of such mercury lamps are the precautions that must be taken to protect the operators from an overexposure to ultraviolet radiation and the long period of time needed for completion of the reaction when a material is exposed to the light radiation from an ultraviolet mercury lamp.

The present invention provides a method for polymerizing a polymerizable ethylenically unsaturated monomer containing at least one polymerizable ethylenically unsaturated group of the structure $>C=C<$ which comprises exposing said monomer to artificial predominantly continuum light radiation from a swirl-flow plasma arc with a radiance of at least 350 watts per square centimeter steradian when integrated throughout the entire spectral range of said continuum light radiation, said predominantly continuum light radiation having at least 70 per cent of the light radiated at a wavelength longer than 4,000 Angstroms and at least some of the light having wavelengths shorter than 4,000 Angstroms.

The present invention also provides a method for curing a curable organic polymer composition which comprises exposing said polymer to artificial predominantly continuum light radiation from a swirl-flow plasma arc with a radiance of at least 350 watts per square centimeter steradian when integrated throughout the entire spectral range of said continuum light radiation, said predominantly continuum light radiation having at least 70 per cent of the light radiated at a wavelength longer than 4,000 Angstroms and at least some of the light having wavelengths shorter than 4,000 Angstroms.

Watts per square centimeter steradian can be abbreviated to $\text{Watts cm}^{-2} \text{sr}^{-1}$. Preferably at least 80 per cent of the light is radiated at a wavelength longer than 4,000 Angstroms. The radiance can vary from 350 watts to 5,000 watts or more per square centimeter steradian. As stated above the source for predominantly continuum light radiation is a swirl-flow plasma arc light radiation apparatus. The equipment for generating predominantly continuum visible light radiation by this means is known and available, with many different forms thereof described in the literature. A highly efficient apparatus for obtaining predominantly continuum light radiation using a swirl-flow plasma arc radiation source is described in U.S. 3,364,387. The apparatus or equipment necessary for generating the light radiation is not the subject of this invention and any source or apparatus can be used.

Any apparatus that operates according to the known principles of the swirl-flow plasma arc radiation source can be used to produce the predominantly continuum visible light radiation used in the processes of this invention. These apparatuses are often known by other terms but those skilled in this art recognize that they emit predominantly continuum visible light radiation. The light source in a 50 kilowatt swirl-flow plasma arc radiation source is an arc only about four inches long enclosed in a quartz envelope about 1.5 inches in diameter. This lamp can be readily replaced and has an acceptably long lifetime. Further, a swirl-flow plasma arc radiation apparatus having a 250-kilowatt rating would be only about two or three times as large as a 50-kilowatt source. Another advantage is the absence of a need for expensive radiation shielding. Precautions required for the artificial light sources include those needed to protect one's eyes from the intense visible light and from the ultraviolet light present to prevent inadvertent sunburn effect on the body.

The term predominantly continuum visible light radiation means radiation which has only a minor part of the energy in peaks of bandwidths less than 100 Angstrom units, at least 70 per cent of the energy at wavelengths longer than 4,000 Angstrom units, with at least 30 per cent of the radiated energy between 4,000 and 7,000 Angstrom units. This type of continuum light radiation is illustrated by the curves shown in Figures 1 to 3. These curves illustrate the predominantly visible light radiation over the range of radiance of from about 350 watts per square centimeter steradian to about 5,000 watts per square centimeter steradian. As is evident from the curves the light radiated is predominantly continuum visible light with very little light emitted as line radiation (band widths less than 100 Angstrom units). It is also evident that at least 70 per cent of the radiated light has a wavelength longer than 4,000 Angstrom units and at least some of the light has wavelengths shorter than 4,000 Å.

Figure 3 is the light radiation curve from an 18 kilowatt argon swirl-flow plasma arc radiation source. The measured radiance was 360 watts per square centimeter steradian and about 92 per cent of the light had a wavelength longer than 4,000 Angstrom units; 33 per cent of the radiated energy was emitted between 4,000 and 7,000 Angstrom units.

Figure 2 is the light radiation from a 60 kilowatt argon swirl-flow plasma arc radiation source. The measured source intensity was about 2,300 watts per square centimeter steradian and about 90 per cent of the light had a wavelength longer than 4,000 Angstrom units; 44 per cent of the radiated energy was emitted between 4,000 and 7,000 Angstrom units.

Figure 3 is the light radiation from a 71 kilowatt argon swirl-flow plasma arc radiation source. The measured source intensity was about 4,860 watts per square centimeter steradian and about 88 per cent of the light had a wavelength longer than 4,000 Angstrom units; 46 per cent of the radiated energy was emitted between 4,000 and 7,000 Angstrom units.

Predominantly continuum visible light radiation is to be distinguished from light radiation generated by low and medium pressure mercury arc ultraviolet light sources. These mercury arcs produce light emission which is primarily line rather than continuum light. As shown in Figure 4, a major part of the light appears in bands narrower than 100 Angstrom units, and much less than 70 per is above 4,000 Angstrom units. Figure 4 is a typical curve for the light radiation from a low pressure mercury arc.

As is known, the predominantly continuum visible light radiation from a swirl-flow plasma arc radiation means is emitted from an arc generated between a pair of electrodes that are lined up axially and encased in a quartz cylinder. In a preferred embodiment a pair of concentric quartz cylinders between which cooling water or gas flows is used. A rare gas, such as argon, krypton, neon or xenon, introduced into the inner cylinder tangentially through an inlet near the inner surface of this cylinder swirls inward to exit through an opening at the tip of each electrode, creating a swirling flow or vortex which restricts the arc to a small diameter. As the high electrical potential applied across the electrodes passes through the gas, a mixture of electrons, positively charged ions and neutral atoms is created. The proper selection of the gaseous medium in which the arc operates determines the wavelength range of the radiated light. All of the gases exhibit well-defined predominantly continuum visible light radiation with diffuse maxima in the region of from 3,500 to 6,000 Angstroms. In addition to predominantly continuum visible light radiation, there is a definite and characteristic line structure associated with each gas at atmospheric pressure. These facts are known in the art. The quartz cylinders can also be partially or wholly enclosed by reflectors to direct the predominantly continuum visible light radiation emanating from the arc to a particular point or direction or geometrical area.

The discovery that the predominantly visible continuum light radiation from, for example, a swirl-flow plasma arc radiation source would polymerize monomers in some instances even in the absence of catalysts or photosensitizers, and that it would crosslink polymer compositions was a completely unexpected and unobvious finding. Even more unexpected and unobvious was the discovery that the time needed to polymerize certain monomers or crosslink a polymer composition with artificial predominantly continuum visible light radiation was only a matter of seconds, or at most several minutes. None of the heretofore known light radiation processes have been capable of achieving such fast rates. The examples in support of this invention show many instances in which crosslinking was achieved in seconds with the predominantly continuum visible light radiation from a swirl-flow plasma arc radiation source versus minutes or even hours with light radiation from conventional low or medium pressure mercury arc sources.

Among the monomers that can be polymerized by the process of this invention are the ethylenically unsaturated monomers containing at least one polymerizable ethylenically unsaturated group of the structure $>C=C<$. The process can be used to polymerize a single monomer or a mixture of two or more monomers throughout the entire concentration ranges possible, selected to suit the scientist's purpose. The monomers can be aliphatic, aromatic, cycloaliphatic, or any variant thereof. Illustrative thereof one can mention the olefinic hydrocarbons containing up to 18 carbon atoms such as ethylene, propylene, butylenes, pentenes, hexenes, dodecene, heptenes, octenes, styrene, 4-methylstyrene, alpha methylstyrene, cyclopentadiene, dicyclopentadiene, butadiene, hexadiene, bicyclo[2.2.1]hept-2-ene, bicyclo[2.2.1]hept-2,5-diene, methylbicyclo[2.2.1]hept-2-ene, cyclohexene, 4-methyl-1-pentene and 5-methyl-1-hexene; acrylic acid and its derivatives, such as acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, methacrylic acid, methyl methacrylate, ethyl methacrylate, ethyl acrylate, 2-ethylhexyl acrylate, butoxyethoxyethyl acrylate and neopentyl glycol diacrylate; the vinyl halides such as vinyl chloride and vinylidene chloride; the vinyl esters such as vinyl acetate, vinyl butyrate and vinyl benzoate; the vinyl ketones such as isopropenyl methyl ketone, vinyl phenyl ketone, vinyl methyl ketone and alpha-chlorovinyl methyl ketone; the vinyl thioethers such as vinyl ethyl sulfide, vinyl p-tolyl sulfide, divinyl sulfide. Other monomers or monomer mixtures which are capable of polymerization by the process of this invention are divinyl sulfone, vinyl ethyl sulfone, vinyl ethyl sulfoxide, vinyl sulfonic acid, sodium vinyl sulfonate, vinyl sulfonamide, vinyl pyridine, N-vinyl pyrrolidone, N-vinyl carbazole, and the like. Other suitable vinyl monomers are readily apparent to the skilled polymer chemist; this listing is illustrative only and not all-inclusive. The preferred monomers include styrene and its derivatives and the acrylyl and methacrylyl compounds and derivatives thereof.

The monomers are polymerized by exposing them either alone or in admixture with known free radical catalysts or photosensitizers or conventional additives, as hereinafter shown useful for crosslinking polymers, to the predominantly continuum visible light radiation such as that emanating from a swirl-flow plasma arc radiation source. The process can be carried out continuously by passing the reaction mixture through a transparent conduit or other means positioned in the radiation area or batchwise by placing the reactants in a suitable container and exposing the container and its contents to the predominantly continuum visible light radiation for a prolonged period of time. One can also coat a substrate, such as metal, wood, glass or composition board, with the monomers, or impregnate or coat a fibrous material, such as paper, textile or fiber, with the monomers and expose the treated material to the predominantly continuum visible light radiation. The temperature can vary from 0°C. to 250°C. or higher, preferably from 20°C. to 100°C., and the pressure can be subatmospheric, atmospheric, or superatmospheric to 10 atmospheres or more (limited solely by equipment properties). In some instances catalysts are not needed, thus producing polymers of higher purity, whereas, in other instances highly reactive catalysts are necessary. The exposure to predominantly continuum visible light radiation can be carried out in air or in an inert gas atmosphere.

The process of this invention can also be used to crosslink polymers. The polymers that can be crosslinked include the crosslinkable synthetic organic polymers such as the polyolefins and modified polyolefins, the vinyl polymers, the polyethers, the polyesters, the polylactones, the polyamides, the polyurethanes, the polyamides, the polyureas, the polysiloxanes, the polysulfides, the polysulfones, the polyformaldehydes, the phenol-formaldehyde polymers, the natural and modified natural polymers and the heterocyclic polymers.

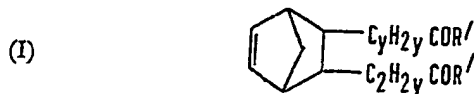
The term polymer as used herein includes the homopolymers and copolymers. The useful crosslinkable polymers include the olefin polymers and copolymers such as polyethylene, polypropylene, polyisobutene, polybutene, poly(ethylene/propylene), poly(ethylene/butene), poly(ethylene/butadiene), poly(ethylene/norbornadiene), poly(ethylene/propylene/norbornadiene), poly(ethylene/propylene/5-methylene-bicyclo[2.2.1]hept-2-ene), poly(ethylene/propylene/5-ethylidene-bicyclo[2.2.1]hept-2-ene), poly(ethylene/vinyl acetate), poly(ethylene/vinyl chloride), poly(ethylene/ethyl acrylate), poly(ethylene/acrylonitrile), poly(ethylene/acrylic acid), poly(ethylene/styrene), poly(ethylene/vinyl ethyl ether), poly(ethylene/vinyl methyl ketone), polybutadiene, polyisoprene, polychloroprene, polycyclopentadiene, poly-1,5-hexadiene, poly(butadiene/isoprene), poly(butadiene/dimethyl butadiene), poly(butadiene/chloroprene), poly(isoprene/isobutylene), poly(butadiene/isobutylene), poly(butadiene/styrene), poly(butadiene/acrylonitrile), poly(butadiene/styrene/acrylonitrile), poly(butadiene/methyl methacrylate), poly(butadiene/butyl acrylate), poly(butadiene/vinyl chloride), poly(isoprene/styrene) and poly(isoprene/2-vinyl pyridine). The olefin

polymers are well known and any such polymers can be used. Also suitable are the vinyl and vinylidene polymers such as poly(vinyl chloride), poly(vinyl bromide), poly(vinylidene chloride), poly(vinyl acetate), poly(vinyl methyl ether), poly(vinyl butyl ether), poly(vinyl methyl ketone), poly(vinyl alcohol), poly(allyl alcohol), polyindene, poly(vinylpyridine), poly(vinylpyrrolidone), poly(vinyl butyral), poly(vinyl chloride), poly(vinyl sulfonic acid), polystyrene, poly(α -methylstyrene), poly(4-chlorostyrene), poly(4-vinyl biphenyl), poly(9-vinyl-anthracene), poly(N-vinyl-carbazole) and poly(N-vinyl-1,2,4-triazole). Further suitable are the acrylic polymers such as poly(acrylic acid), poly(methyl acrylate), poly(ethyl acrylate), polyacrylonitrile, polyacrylamide, polyacrolein, poly(methacrylic acid), poly(methyl methacrylate), poly(ethyl methacrylate), polymethacrylonitrile, poly(N,N-dimethyl acrylamide), poly(methacrylamide), poly(9-acrylylcarbazole), poly(α -methacrolein), poly(diacrylalmethane), poly(acrylic anhydride) and poly(methacrylic anhydride). In addition, the polyesters and polyamides such as polycaprolactone, poly(caprolactone/vinyl chloride), poly(ethylene glycol terephthalate), poly(hexamethylene succinate), poly(hexamethylene maleate), poly(hexamethylene carbonate), poly(caprolactam), poly(hexamethylene adipamide), and the like, are useful. The polyethers such as poly(glutarialdehyde), polyethylene oxide, polypropylene oxide, poly(tetrahydrofuran), polycyclohexene oxide, copolymers of ethylene oxide and propylene oxide with starters containing reactive hydrogen atoms such as the mixed copolymer using ethylene glycol, glycerol or sucrose, as the starter. Also suitable are the known polyureas and polyurethanes as described in "Polyurethanes: Chemistry and Technology", Volumes I and II, Saunders and Frisch, published by Interscience Publishers, as well as the natural and modified natural polymers such as gutta percha, cellulose, methyl cellulose, starch, silk, wool, and the like, and the siloxane polymers and copolymers. The polysulfides and polysulfones such as poly(thiocarboxyl fluoride), poly(ethylene dichloride-co-sodium tetrasulfide), poly(ethylene sulfide), poly(ethylene sulfone), poly(styrene sulfone), poly(1-pentyne sulfone), poly(butadiene sulfone), poly(isoprene sulfone). The formaldehyde polymers such as poly-formaldehyde, formaldehyde resins such as phenol-formaldehyde, melamine-formaldehyde, urea-formaldehyde, aniline-formaldehyde and acetone-formaldehyde. The heterocyclic polymers such as poly(benzimidazoles), poly(alkylene-5,5'-dibenzimidazoles), poly(arylene-5,5'-benzimidazoles), poly(pyromellitimides), poly(benzoxazoles), poly(oxadiazoles), poly(dithiazoles), poly(benzothiazoles), poly(piperazines) and poly(quinoxalines).

The polymers can be crosslinked by the process of this invention by irradiating the polymer, a solution thereof in an inert solvent, or a suspension, dispersion or emulsion thereof with predominantly continuum visible light radiation. A particularly valuable use is the curing and crosslinking of 100 per cent solids coating compositions or compositions wherein a polyester, a polyurethane, an acrylic polymers, a styrene polymer, an olefin polymer, a vinyl polymer, a siloxane polymer, and the like, is compounded with reactive monomers to form coating compositions essentially free of non-reactive volatile solvents. Many of these coating compositions are known in the art, reference herein being made to U.S. 3,392,176. However, this invention is not restricted to 100 per cent solids coating compositions; it can be used to cure any crosslinkable coating composition or polymer, whether or not a vaporizable solvent is present.

Of particular utility are the 100 per cent solids coating compositions produced with certain organic polymers containing the norbornenyl group, particularly polyesters containing the norbornenyl group, and certain high boiling acrylyl esters. 100 per cent solids coating compositions are compositions essentially free from volatile and inert liquid vehicles. These liquid coating compositions have been cured by the process of this invention to solid film coatings in seconds. Generally, the coating compositions contain from 5 to 95 per cent by weight, preferably from 40 to 70 per cent by weight of the polyester or polymer containing the norbornenyl group and from 95 to 5 per cent by weight, preferably from 30 to 60 per cent by weight of one or more high boiling acrylyl esters. Most preferably the acrylyl ester concentration is from 25 to 55 per cent by weight of the composition. The compositions can contain pigments, fillers, photosensitizers, crosslinkers, and the like, all of which are known to be useful in this art.

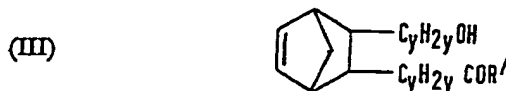
The polyesters containing the norbornenyl group are produced by the known procedures using as the norbornene compound a norbornene dicarboxylic acid, its anhydride, ester, ester chloride or ester dichloride of the formula—



5 or a dihydroxyl norbornene of the formula—



or a norbornene hydroxyl acid, ester, or ester chloride of the formula—



in which y has a value of 0 to 5 and R' is hydroxyl or alkoxyl having from 1 to 3 carbon atoms or chlorine.

Polyesters can be produced by the self-condensation of the norbornene hydroxyl acids (III), alone or with other hydroxyl acid compounds. Polyesters can also be produced by the condensation of a mixture of the norbornene dicarboxylic acid compounds (I) with dihydroxyl norbornenes (II). In addition the polyesters can be produced by the reaction of the norbornene dicarboxylic acid compounds (I) with other aliphatic diols, alone or in admixture with other known dicarboxylic acids or esters. Further, the polyesters can be produced by the reaction of the dihydroxyl norbornenes (II) with other known dicarboxylic acids, either alone or in admixture with other known aliphatic diols. These procedures are known in the art.

In a typical method for the production of polyesters, the calculated amounts of carboxylic acid compounds, hydroxyl compounds and catalyst are charged to a reactor and heated in an inert atmosphere at a temperature below the decomposition temperature of the initial reactants. This is preferably from 150°C. to 250°C. It is conventional to use an excess of the least expensive compound, which excess can readily be determined since the reaction between the hydroxyl group and the carboxyl group proceeds in a stoichiometric ratio to form the ester group. If desired the pressure can be reduced to remove low boiling components and to complete the polycondensation reaction. The total esterification time is known to vary since it is dependent upon such variables as the catalyst, starting materials, pressure, temperature and size of batch. The catalyst is generally present at a concentration of from 0.001 per cent to 1 per cent, preferably from 0.005 per cent to 0.3 per cent, based on the weight of the carboxylic acids charged. Among the known polyesterification catalysts one can mention antimony oxide, zinc acetate, manganese acetate, cobaltous acetate, zinc succinate, zinc borate, magnesium methoxide, sodium methoxide, barium oxide, cadmium formate, lithium, dibutyltin-oxide, tetraisopropyl titanium silicate and tetrabutyl titanate.

Illustrative of conventional diols useful for the production of the polyesters are the aliphatic diols represented by the general formula $\text{HOC}_n\text{H}_{2n}\text{OH}$ in which n is an integer of from 2 to 10, such as ethylene glycol, propylene glycol, trimethylene glycol, neopentylene glycol, pentamethylene glycol, hexamethylene glycol and decamethylene glycol. Also suitable are 1,4 - cyclohexanedimethanol, diethylene glycol, p - xylylene glycol, 4 - hydroxybenzyl alcohol, 2,2 - dimethyl - 3 - hydroxypropyl 2,2 - dimethyl - 3 - hydroxypropionate and the like. It is known that any diol of an aliphatic nature, whether or not it contains aromatic nuclei can be used in the production of polyesters. Thus, the term aliphatic diols includes all those diols of an aliphatic nature which are known in the art to be suitable.

The use of the norbornenyl acid chlorides in producing polyesters is advantageous since lower temperatures can be used in the condensation reaction. Thus, polyesters can be produced by the condensation of a norbornene dicarboxylic acid chloride (I) with dihydroxyl norbornenes (II). In addition the polyesters can be produced by the reaction of the norbornene dicarboxylic acid chloride (I) with other aliphatic diols, alone or in admixture with other known dicarboxylic acid chlorides. Further, the poly-

esters can be produced by the reaction of the dihydroxyl norbornenes (II) with other known dicarboxylic acid chlorides, either alone or in admixture with other known aliphatic diols.

A typical method for the production of polyesters from dicarboxylic acid chlorides and hydroxyl compounds combines approximately equivalent quantities of each in a reaction medium or solvent containing an acid-binding agent. The esterification is accomplished by heating the mixture to an elevated temperature. Since the reaction takes place under very mild conditions especially high temperatures are not necessary, 65—150°C., for example, being the preferred range of reaction temperatures.

The reaction medium may be a diluent or solvent; it is preferable that at least the starting materials be dissolved at the reaction temperature. Suitable as a reaction medium or solvent are aliphatic and aromatic hydrocarbons such as cyclohexane, heptane, benzene, toluene, tetrahydronaphthalene or cumene, halogenated hydrocarbons such as, chloroform, tetrachloroethylene, monochlorobenzene, orthodichlorobenzene, trichlorobenzene, ethers such as diphenyl ether, diisopropyl ether, N,N-dialkyl amides such as dimethyl formamide, dimethyl acet amide and alkyl sulfoxides such as dimethyl sulfoxide and tetramethylene sulfoxide. The N,N-dialkyl amides are preferred owing to their catalytic effect and favorable solvent power.

As acid binding agents, there are suitable, for example, pyridine and its homologues, furthermore N,N-dialkyl anilines, especially N,N-diethyl aniline, isoquinoline and other stable heterocyclic nitrogen bases. Aliphatic or cycloaliphatic tertiary amines can also be used, for example, triethylamine, diethylene triamine, N-methylpiperidine and N-butylpyrrolidine. Also non-basic hydrogen halide acceptors may be used such as acrylonitrile, alkyl or arylsulfethyleneimide, and the like.

The conventional carboxylic acids useful for the production of the polyesters are well known to those skilled in the art. The most widely used is terephthalic acid and the dialkyl esters thereof, such as dimethyl terephthalate, in which the alkyl group contains from 1 to 5 carbon atoms. Other known dicarboxylic acids or their esters include isophthalic acid, p,p'-diphenylcarboxylic acid, p,p'-dicarboxydiphenyl ethane, p,p'-dicarboxydiphenyl hexane, p,p'-dicarboxydiphenyl sulfide, p,p'-dicarboxydiphenyl ether, p,p'-dicarboxyphenoxy butane, 2,6-dinaphthalene dicarboxylic acid. These aromatic acids can be used alone or in admixture, and up to 20 per cent by weight of the aromatic acid can be replaced by an aliphatic dicarboxylic acid or ester thereof, such as adipic acid, succinic acid, sebacic acid and dimethyl 1,20-eicosane dioate.

Illustrative of known hydroxy acids that can be used in the production of the polyesters one can mention 4-hydroxybenzoic acid, 4-hydroxybutyric acid, 10-hydroxydecanoic acid, 3-hydroxy-2,2-dimethylpropionic acid, as well as the esters thereof.

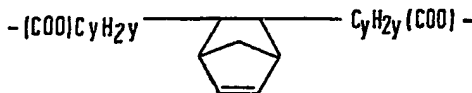
Suitable norbornene compounds for the production of the polyesters include 5,6-dicarboxybicyclo[2.2.1]hept-2-ene and the anhydride thereof; the dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, ditertiarybutyl, and dipentyl esters of 5,6-dicarboxybicyclo[2.2.1]hept-2-ene; the dicarboxyalkylbicyclo[2.2.1]hept-2-enes such as 5,6-dicarboxymethylbicyclo[2.2.1]hept-2-ene, 5,6-di-(2-carboxyethyl)bicyclo[2.2.1]hept-2-ene, 5,6-di-(3-carboxypropyl)bicyclo[2.2.1]hept-2-ene, 5,6-di-(2-carboxypropyl)bicyclo[2.2.1]hept-2-ene, the 5,6-dicarboxybutylbicyclo[2.2.1]hept-2-enes, 5-carboxyethyl-6-carboxypropylbicyclo[2.2.1]hept-2-ene, 5-carboxymethyl-6-carboxypentylbicyclo[2.2.1]hept-2-ene, 5-carboxy-6-carboxymethylbicyclo[2.2.1]hept-2-ene, the 5,6-dicarboxypentylbicyclo[2.2.1]hept-2-enes, 5,6-di(carboxy-2-ethylhexyl)bicyclo[2.2.1]hept-2-ene, the 5,6-dicarboxydecylbicyclo[2.2.1]hept-2-enes; the alkyl esters of said 5,6-dicarboxyalkylbicyclo[2.2.1]hept-2-enes; 5,6-dihydroxybicyclo[2.2.1]hept-2-ene; the lower fatty acid esters such as the acetoxyl, propionoxyl, butyryloxy, pentanoyloxy esters of 5,6-dihydroxybicyclo[2.2.1]hept-2-ene; the 5,6-dihydroxyalkylbicyclo[2.2.1]hept-2-enes such as 5,6-dihydroxymethylbicyclo[2.2.1]hept-2-ene, 5,5-dihydroxymethylbicyclo[2.2.1]hept-2-ene, 5,6-di-(2-hydroxyethyl)bicyclo[2.2.1]hept-2-ene, 5-hydroxy-6-hydroxyethylbicyclo[2.2.1]hept-2-ene, 5-hydroxy-methyl-6-hydroxybutylbicyclo[2.2.1]hept-2-ene, the 5,6-dihydroxypropylbicyclo[2.2.1]hept-2-enes, the 5,6-dihydroxypentylbicyclo[2.2.1]hept-2-enes, the 5,6-dihydroxybutylbicyclo[2.2.1]hept-2-enes, the 5,6-dihydroxyisopropylbicyclo[2.2.1]hept-2-enes; the lower fatty acid esters of said 5,6-dihydroxyalkylbicyclo[2.2.1]hept-2-enes; 5-hydroxy-6-carboxybicyclo[2.2.1]hept-2-ene; the lower mono- and di-esters of said 5-hydroxy-6-carboxybicyclo[2.2.1]hept-2-ene such as 5-carboxy-6-acetoxybicyclo[2.2.1]hept-2-ene, 5-carboxy-6-propionoxybicyclo[2.2.1]hept-2-ene, 5-carboxy-6-butyryloxybicyclo[2.2.1]hept-2-ene, 5-acetoxyl-6-carbomethoxybicyclo[2.2.1]hept-2-ene, 5-acetoxy-

6 - carbopentoxybicyclo[2.2.1]hept - 2 - ene, 5 - pentanoyloxy - 6 - carbomethoxybicyclo[2.2.1]hept - 2 - ene, 4 - butyryloxy - 6 - carbopropoxybicyclo[2.2.1]hept - 2 - ene, 5 - hydroxy - 6 - carbomethoxybicyclo[2.2.1]hept - 2 - ene, 5 - hydroxy - 6 - carbopropoxybicyclo[2.2.1]hept - 2 - ene, 5 - hydroxy - 6 - carbopentoxybicyclo[2.2.1]hept - 2 - ene; the 5 - hydroxyalkyl - 6 - carboxyalkylbicyclo[2.2.1]hept - 2 - enes such as 5 - hydroxymethyl - 6 - carboxymethylbicyclo[2.2.1]hept - 2 - ene, 5 - hydroxymethyl - 6 - carboxypentylbicyclo[2.2.1]hept - 2 - ene, 5 - hydroxypentyl - 6 - carboxypentylbicyclo[2.2.1]hept - 2 - ene, 5 - hydroxypropyl - 6 - carboxypropylbicyclo[2.2.1]hept - 2 - ene; the lower mono- and di-esters of said 5 - hydroxyalkyl - 6 - carboxyalkylbicyclo[2.2.1]hept - 2 - enes such as 5 - acetoxymethyl - 6 - carboxymethylbicyclo[2.2.1]hept - 2 - ene, 5 - butyryloxymethyl - 6 - carboxyethylbicyclo[2.2.1]hept - 2 - ene, 5 - acetoxypentyl - 6 - carboxypropylbicyclo[2.2.1]hept - 2 - ene, 5 - acetoxymethyl - 6 - carbomethoxymethylbicyclo[2.2.1]hept - 2 - ene, 5 - propionyxyethyl - 6 - carbomethoxyethylbicyclo[2.2.1]hept - 2 - ene, 5 - acetoxypentyl - 6 - carbobutoxypropylbicyclo[2.2.1]hept - 2 - ene, 5 - hydroxymethyl - 6 - carbomethoxymethylbicyclo[2.2.1]hept - 2 - ene, 5 - hydroxypropyl - 6 - carbomethoxymethylbicyclo[2.2.1]hept - 2 - ene, 5 - hydroxypentyl - 6 - carbopropoxybicyclo[2.2.1]hept - 2 - ene, 5 - hydroxyethyl - 6 - carbobutoxymethylbicyclo[2.2.1]hept - 2 - ene, 5 - hydroxyethyl - 6 - carbomethoxypentylbicyclo[2.2.1]hept - 2 - ene.

These compounds are readily produced by the Diels-Alder reaction of cyclopentadiene with the appropriate ethylenically unsaturated compound as disclosed in United States Patent No. 2,340,908.

A preferred polyester is that which is the reaction product of 5,6 - dicarboxybicyclo[2.2.1]hept - 2 - ene or its anhydride with the diol 2,2 - dimethyl - 3 - hydroxypropyl 2,2 - dimethyl - 3 - hydroxypropionate wherein the diol is used alone or in admixture with one or more known polyhydroxyl compounds.

The norbornenyl polyesters are characterized by the presence in the polymer molecule of the group:



wherein the ester linkages can be either $-\overset{\overset{O}{\parallel}}{C}-O-$ or $-O-\overset{\overset{O}{\parallel}}{C}-$, depending on whether the norbornene starting compound was carboxylic in nature or hydroxylic in nature.

The norbornenyl group can be formed in situ in the polyester, if one wishes to do so. These procedures are known to those skilled in the art and are illustrated by the following description. A polyester was produced by the conventional procedure by reacting maleic anhydride and 2,2 - dimethyl - 3 - hydroxypropyl 2,2 - dimethyl - 3 - hydroxypropionate at about 200°C. using xylene as the solvent medium. Thereafter, dicyclopentadiene is reacted with the polyester by a Diels-Alder reaction of the cyclopentadiene generated to form the norbornenyl group in the polyester chain. While this illustration shows the use of maleic anhydride as the unsaturated site for the formation of the norbornenyl group, it is obvious that the unsaturated site can be introduced into the polyester via any unsaturated carboxylic compound or any unsaturated hydroxyl compound that contains an unsaturated site that will undergo the Diels-Alder reaction with cyclopentadiene or dicyclopentadiene.

The greater the concentration of norbornenyl group in the polyester the faster is the rate at which the coating composition will cure upon exposure to high intensity irradiation. Thus, when a mixture of carboxylic compounds is used, it is preferred to have the norbornenyl-containing compound present in major molar concentration.

Illustrative of the polyesters containing the norbornenyl group that can be used in producing the 100 per cent solids coating compositions of this invention are the polyesters produced from the following mixtures of reactants; the figures in the parenthesis represent the mole per cent of each compound of that particular class present in the reaction mixture.

1. 5,6-dicarboxybicyclo[2.2.1]hept-2-ene; ethylene glycol.
2. 5,6-dicarboxybicyclo[2.2.1]hept-2-ene (75)
dimethylterephthalate (25)
ethylene glycol.
3. dimethylester of 5,6-dicarboxybicyclo[2.2.1]hept-2-ene (90)

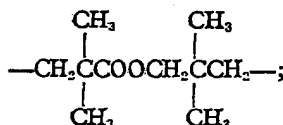
	dimethylterephthalate (10)	
	ethylene glycol.	
5	4. 5,6-dicarboxymethylbicyclo[2.2.1]hept-2-ene (80)	
	dimethylterephthalate (20)	
	ethylene glycol.	5
	5. diethylester of 5,6-dicarboxymethylbicyclo[2.2.1]hept-2-ene (70)	
	dimethylterephthalate (30)	
	ethylene glycol.	
10	6. 5,6-dihydroxybicyclo[2.2.1]hept-2-ene dimethylterephthalate.	
	7. 5,6-diacetoxymethylbicyclo[2.2.1]hept-2-ene isophthalic acid	10
	8. 5,6-dihydroxybicyclo[2.2.1]hept-2-ene terephthalic acid (90)	
	p,p'-diphenylcarboxylic acid (10)	
	9. 5,6-dihydroxybicyclo[2.2.1]hept-2-ene (75)	
	ethylene glycol (25)	
15	dimethylterephthalate.	15
	10. 5,6-dihydroxymethylbicyclo[2.2.1]hept-2-ene (70)	
	ethylene glycol (30)	
	dimethylterephthalate.	
20	11. 5,6-diacetoxymethylbicyclo[2.2.1]hept-2-ene (90)	
	ethylene glycol (10)	20
	dimethylterephthalate.	
	12. 5-hydroxy-6-carboxybicyclo[2.2.1]hept-2-ene.	
	13. 5-hydroxy-6-carboxybicyclo[2.2.1]hept-2-ene (80)	
	3-hydroxypropionic acid (20).	
25	14. 5-carboxy-6-acetoxymethylbicyclo[2.2.1]hept-2-ene (90)	25
	7-hydroxypentanoic acid (10).	
	15. 5-acetoxy-6-carbomethoxybicyclo[2.2.1]hept-2-ene (50)	
	p-hydroxybenzoic acid (50)	
30	16. 5-hydroxy-6-carbomethoxybicyclo[2.2.1]hept-2-ene (60)	
	6-hydroxyhexanoic acid (40).	30
	17. 5-hydroxymethyl-6-carboxymethylbicyclo[2.2.1]hept-2-ene (50)	
	6-hydroxyhexanoic acid (50).	
	18. 5-acetoxymethyl-6-carboxymethylbicyclo[2.2.1]hept-2-ene (50)	
	6-hydroxyhexanoic acid (50).	
35	19. 5-acetoxymethyl-6-carbomethoxymethylbicyclo[2.2.1]hept-2-ene (60)	35
	7-hydroxypentanoic acid (40).	
	20. 5-hydroxymethyl-6-carbomethoxymethylbicyclo[2.2.1]hept-2-ene (50)	
	7-hydroxypentanoic acid (50).	
40	21. 5,6 - dicarboxybicyclo[2.2.1]hept - 2 - ene 5,6 - dihydroxybicyclo[2.2.1]-	
	hept - 2 - ene.	40
	22. 5,6 - dicarboxymethylbicyclo[2.2.1]hept - 2 - ene 5,6 - dihydroxybicyclo-	
	[2.2.1]hept - 2 - ene.	
	23. diethylester of 5,6 - dicarboxyethylbicyclo[2.2.1]hept - 2 - ene 5,6 - di-	
45	hydroxybicyclo[2.2.1]hept - 2 - ene.	45
	24. 5 - hydroxy - 6 - carboxybicyclo[2.2.1]hept - 2 - ene 5 - hydroxy - 6 - carbo-	
	propoxybicyclo[2.2.1]hept - 2 - ene.	
	25. bicyclo[2.2.1]hept - 5 - en - 2,3 - dicarboxylic acid anhydride 2,2 - dimethyl-	
	3 - hydroxypropyl 2,2 - dimethyl - 3 - hydroxypropionate.	
50	26. bicyclo[2.2.1]hept - 5 - en - 2,3 - dicarboxylic acid anhydride 2,2 - dimethyl-	
	3 - hydroxypropyl 2,2 - dimethyl - 3 - hydroxypropionate (94).	50
	Pentaerythritol (6).	

The polyesters can be modified by reaction thereof with an isocyanate. This was found to yield modified polyesters that when used in 100 per cent solids coating compositions produced compositions that cured to solids in a much shorter period of time. The preferred are the polyisocyanates such as diisocyanates containing the norbornenyl group, e.g., bis(2 - isocyanatoethyl) bicyclo[2.2.1]hept - 5 - en - 2,3 - dicarboxylate, bicyclo[2.2.1]hept - 5 - en - 2,3 - diisocyanate and bicyclo[2.2.1]hept - 5 - en - 2,3 - di(methylisocyanate). In addition, however, conventional known isocyanates can be used, for example, 1,6 - hexamethylenediisocyanate, methylcyclohexane - 2,4 - diisocyanate, methylcyclohexane - 2,6 - diisocyanate, 3,5,5 - trimethylcyclohexane - 1,3 - diisocyanate, and the like. The reaction of an isocyanate compound with a polyester is a well known chemical reaction and requires no further explanation to enable one skilled in the art to conduct it.

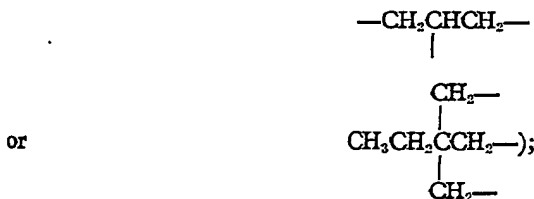
The high boiling acrylyl compounds that are useful in this invention can contain more than one acrylyl group in the molecule; they are represented by the general formula:



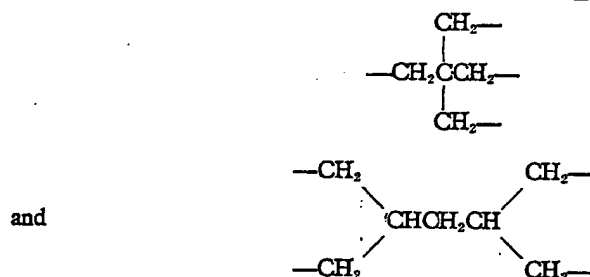
- 5 wherein R''' can be hydrogen or methyl; z is an integer having a value of from 1 to 4 and is the valence of R''; and R'' can be a monovalent group such as hydrogen; alkyl of from 1 to 18 carbon atoms (e.g. methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, pentyl, hexyl, 2-methylhexyl, 2,3-dimethylbutyl, neopentyl, heptyl, neohexyl, 3,3-dimethylpentyl, octyl, 2-ethylhexyl, nonyl and decyl); hydroxyalkyl having up to 10 carbon atoms (eg hydroxymethyl, 2-hydroxyethyl, hydroxyisopropyl, 2-hydroxy-1-propyl, hydroxyhexyl and hydroxydecyl); alkoxyalkyl having up to 15 carbon atoms (eg methoxymethyl, methoxybutyl, methoxydecyl, ethoxyethyl, ethoxyoctyl, butoxyethyl, butoxypropyl, hexoxyethyl, decoxyethyl and decoxypentyl); haloalkyl wherein the alkyl group has up to 15 carbon atoms as defined above and the halogen can be fluorine, chlorine, bromine or iodine (eg chloromethyl, chlorodecyl, fluoroethyl, bromethyl, iodo-
15 methyl, dichloroethyl and perfluoroisopropyl trichlorobutyl); cyano; cyanoalkyl wherein the alkyl group has up to 15 carbon atoms as defined above (eg cyanomethyl, cyanoalkyl, cyanobutyl and cyanodecyl); epoxyalkyl wherein the alkyl group has up to 15 carbon atoms as defined above (e.g. glycidyl, 4,5-epoxypentyl and 2,3-epoxycyclohexyl); aryl (e.g. phenyl, xylyl, tolyl, naphthyl, naphthal and benzyl); aryloxyalkyl wherein the alkyl group has up to 15 carbon atoms as defined above (e.g. 2-phenoxyethyl, 10-
20 phenoxydecyl, 2-tolyloxyethyl and 2-naphthylloxyethyl); trialkoxysilyloxyalkyl wherein the alkoxy group has from 1 to 5 carbon atoms and the alkyl group has up to 15 carbon atoms as defined above (e.g. trimethoxysilyloxymethyl, trimethoxysilyloxypropyl, trimethoxysilyloxydecyl, triethoxysilyloxyethyl, triethoxysilyloxybutyl, tripropoxysilyloxyethyl and tributoxysilyloxyethyl); —CONR'''' wherein R'''' can be hydrogen or hydrocarbyl having up to 15 carbon atoms (e.g. N-methyl, N-ethyl, N-propyl, N-butyl, N-decyl, N,N-dimethyl, N,N-diethyl, N,N-diisobutyl, N-cyclohexyl, N,N-dicyclohexyl, N-phenyl, N-naphthyl, N-methyl-N-phenyl, N,N-diphenyl, N-benzyl, N,N-dibenzyl and N-tolyl); dicyclopentenyl; bicyclo[2.2.1]hept-2-en-5-yl; bicyclo[2.2.1]hept-2-en-5-ylalkyl, wherein the alkyl group has from 1 to 4 carbon atoms (e.g. bicyclo[2.2.1]hept-2-en-5-ylmethyl and bicyclo[2.2.1]hept-2-en-5-ylpropyl); R'' can also be a polyvalent group such as a divalent —C_pH_{2p}— group wherein p has a value of from 1 to 10 (e.g. methylene, ethylene, propylene, isopropylene, butylene, hexylene, 2,2-dimethylbutylene, 2-ethylhexylene and decylene);
35 —C_wH_{2w}(OC_vH_{2v})_v— wherein w has a value of from 2 to 4 and v has a value of from 1 to 5000 and the oxyalkylene portion thereof can be oxyethylene, oxypropylene, 2-oxypropylene, oxybutylene, or mixed oxyalkylene groups in the same molecule;



- 40 a trivalent aliphatic hydrocarbon of the formula C_qH_{2q-1} wherein q has a value of from 3 to 10 (e.g. 40



- 45 or a tetravalent aliphatic hydrocarbon of the formula C_sH_{2s-2} wherein s has a value of from 4 to 10 (eg. 45



The acrylyl compounds defined by Formula IV above are well known in the art and many of them are described in "Vinyl and Related Polymers" by C. E. Schildknecht, published in 1952 by John Wiley and Sons. The common knowledge of these compounds makes the specific naming thereof in this specification unnecessary in view of the extensive description set forth above.

The 100 per cent solids coating compositions are produced by mixing the selected components thereof by conventional known methods. The blend can be heated, if desired, to facilitate mixing.

The coating compositions can be applied by conventional means and including spray, curtain, dip, pad and roll-coating techniques and may, if desired, be dried under ambient or oven conditions to provide coating films on the substrate. The substrate can be any composition, e.g. wood, metal, paper, plastic, fabric, fiber, ceramic, concrete, plaster and glass.

Also, the process of this invention can be used to crosslink the other crosslinkable norbornenyl containing polymers disclosed in U.K. Patent Application No. 1874/69 (Serial No. 1,263,294). The polymers disclosed in U.K. Patent Application No. 1874/69 (Serial No. 1,263,294) include polyamides, polyethers, polyurethanes, polyureas and vinyl polymers wherein the norbornenyl group is part of the backbone of the polymer chain; the application also discloses polymers wherein the norbornenyl group is pendant to the polymer backbone. Said application fully discloses the polymers and the methods for their production.

While reference has been made herein to 100 per cent solids coating compositions, it is to be understood that conventional coating compositions can also be used to coat articles and the coating is crosslinked after evaporation of the volatile solvent. Further, is also to be understood that the coating compositions can contain a free radical initiator or other catalyst.

Crosslinking by the processes of this invention can be carried out at any temperature of from 0°C., or lower, to 150°C., or higher. Neither the temperature nor the pressure are critical. An inert atmosphere can be maintained in the irradiation area, but this is not critical. The irradiation time can vary from as little as 0.01 second to 10 minutes, or more. However, it has been found that maximum crosslinking is achieved in 0.1 seconds to 60 seconds. The time required for optimum crosslinking or curing will vary with the specific reactants and with the properties desired by the scientist in the final product. The polymer composition can be positioned at any reasonable distance from the arc of the swirl-flow plasma arc radiation source; the distance will be determined by the area to be irradiated, the polymer system employed and the time that the sample is to be exposed. It has been generally observed that the curing time decreases rapidly as the distance between the polymer and the arc decreases. In the laboratory, distances of less than five feet have been employed, but the distance can be greater than this in large scale commercial operations.

A single source generating essentially predominantly continuum visible light radiation, for example, a swirl-flow plasma arc radiation means can be used or one may choose to use two or more sources of predominantly continuum light radiation. Generally, the more intense the predominantly continuum visible light radiation, the faster will be the cure. Further, where a large object, such as a coated building panel, household appliance, or automobile body, is involved a bank of predominantly continuum visible light radiation sources can be positioned around the object as it is conveyed through the area and exposed to the light radiation in order to rapidly crosslink the coating on the complete surface.

The process of this invention can be used to irradiate shaped polymers, for example, self-supporting films, fibers, molded or extruded shapes, to crosslink the polymer, as well as laminates of the polymer on solid substrates such as wood, paper, fabric, metal, glass, mineral and plastic. It can also be used to crosslink the polymer

after a fibrous material has been impregnated or coated therewith.

In those instances wherein a solid polymer cannot be produced by the previously known methods, exposure to the predominantly continuum visible light radiation from the swirl-flow plasma arc radiation source has converted liquid, low molecular weight polymers to solid self-supporting films. This can be done continuously by casting a film of the liquid polymer on a substrate, e.g. a moving belt, passing the film on the belt under the predominantly continuum visible light radiation and stripping off the solid film.

The predominantly continuum visible light radiation emanating from the artificial light generating means can also be used to irradiate polyethylene foam structures to crosslink the polyethylene and improve the physical and mechanical properties of the polyethylene foam article. This is also true of other polyolefin foams.

Insulation on electrical conductors, wherein the conductor is sodium, copper, aluminum, silver, or any other metal or alloy, can be crosslinked with the predominantly continuum visible light radiation from the radiation source by exposing the insulated conductor to the predominantly visible continuum light radiation. It was found that polyethylene insulation cured after about 60 seconds exposure to the predominantly continuum visible light radiation. An insulated sodium conductor having a one quarter inch thick insulation of the copolymer of a mixture of ethylene and about one mole per cent of bicyclo[2.2.1]hept-2,5-diene and containing 0.5 weight per cent p-methoxybenzophenone as photosensitizer reached its optimum crosslinking after being exposed for about 12 seconds to the predominantly continuum visible light radiation from an argon 30 kilowatt swirl-flow plasma arc radiation source. Similar results are obtained with polyethylene insulations having densities of from about 0.915 to about 0.97 g./cc., or higher. Polypropylene can also be used as the insulant.

Curing or crosslinking of the crosslinkable polymers can be carried out on mixtures thereof with known crosslinkers such as the dinorbornene compounds disclosed and described in U.K. Patent Application No. 49988/69 (Serial No. 1299446). It is to be understood that any of the known crosslinkers can be used including but not limited to the polyunsaturated crosslinkers such as triallyl cyanurate, allyl acrylate, allyl methacrylate, diallyl terephthalate, N,N'-methylene diacrylamide, 1,2-ethylene diacrylate, diallyl maleate, diallyl fumarate, 1,2-ethylene dimethacrylate, hexamethylene bis maleimide, triallyl phosphate, trivinyl trimellitate, divinyl adipate, trimethylolpropane triacrylate, glyceryl trimethacrylate, diallyl succinate and divinylbenzene, can also be used. The crosslinkers can be present at concentrations as high as 90 per cent, or more, but preferably less than 50 per cent.

Further the rate and extent of crosslinking can be enhanced by blending the crosslinkable polymer with a photosensitizer or free radical generator. Illustrative of known photosensitizer compounds one can mention acetophenone, propiophenone, benzophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3- or 4-methylacetophenone, 3- or 4-pentylacetophenone, 3- or 4-methoxyacetophenone, 3- or 4-bromoacetophenone, 3- or 4-allylacetophenone, 6-diacetylbenzene, 3- or 4-methoxybenzophenone, 3- or 4-methylbenzophenone, 3- or 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4-chloro-4'-benzylbenzophenone, 3-chloroxanthone, 3,9-dichloroxanthone, 3-chloro-8-nonylxanthone, 3-methoxyxanthone and 3-iodo-7-methoxyxanthone. As free radical initiators, one can mention the dialkyl peroxides (cyclic or acyclic), diaryl peroxides, hydroperoxides, peracids, peresters, azo compounds, and other known free radical sources. Illustrative thereof are di-tert-butyl peroxide, benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, t-butylhydroperoxide, 2,5-dimethyl-2,5-bis(hydroperoxy)-hexane, peracetic acid, perbenzoic acid, t-butyl peroxy-pivalate, t-butyl peracetic and azo-bis-isobutyronitrile.

As is obvious, one can use one or more photosensitizers or free radical initiators or combinations of each type or of both types. It is to be understood that any known photosensitizer or free radical initiator can be used; one is not restricted to those specifically referred to above. The amount of photosensitizer or free radical initiator can vary from 0.01 to 20 weight per cent of the polymer. A preferred amount is from 0.1 to 5 weight per cent, and most preferred is from 0.5 to 2 weight per cent. In some instances, a synergistic effect is noted by the use of mixtures. For example, the mixture of benzophenone and 2,4-dichlorobenzoyl peroxide to crosslink siloxane polymers or the mixtures of benzophenone and triethanolamine (which for purposes of this invention is considered a free radical initiator) or 4-methoxybenzophenone and triethanolamine to crosslink 100 per cent solids coating compositions containing a high boiling acrylate monomer and a polymer such as a polyester or a polyurethane.

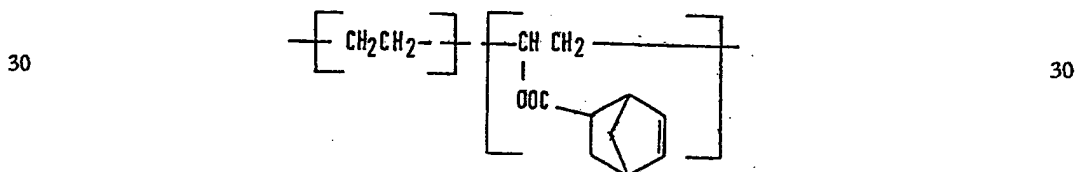
In the following examples, which are illustrative of the invention, the following test procedures were used to evaluate the products.

Tests

5	Hardness (Shore A Units)	ASTM D2240—64T	
	Elongation, %	ASTM D638 —67T	5
	Tensile strength, psi	ASTM D638 —67T	
	Set at break, %	ASTM D638 —67T	
	Melt index, dgm/min	ASTM D1248—68	
	Density, g./cc.	ASTM D1248—68	
10	Stiffness, psi	ASTM D638 —67T	10
	Tensile modulus, psi	ASTM D638 —67T	
	Tensile strength on paper using a two inch strip of paper, psi—ASTM No. 1682—59T		

Example 1

15	An ethylene/vinyl acetate copolymer, 300 grams, having about 16.2 weight per cent vinyl acetate was dissolved in 1400 grams of toluene by heating to the reflux temperature. Methanol, 129 grams, was added at 70°C., and then 23.2 grams of a 25 per cent methanolic solution of sodium methoxide was added. The solution was re-	15
20	fluxed for several hours, cooled, poured into methanol and filtered to recover the hydrolyzed copolymer. This was washed with methanol until neutral and dried in a vacuum oven. The hydrolyzed copolymer, 100 grams (equivalent to 0.125 mole of vinyl alcohol), 500 ml. of benzene and 10 ml. of pyridine were charged to a one liter flask and 50 ml. of the solution was azeotropically distilled to remove traces of water. Over a 15 minute period 20.5 grams of 5-chloroformylbicyclo[2.2.1]hept-2-ene were added	20
25	to the refluxing solution and then refluxing was continued for another hour. The solution was cooled to 40°C. and methanol was slowly added until it became cloudy; then two liters of methanol were quickly added. The ethylene/vinyl bicyclo[2.2.1]-hept-2-en-5-carboxylate copolymer was filtered, washed with methanol and dried; it contained the following units in the polymer chain:	25



35	Blends of this copolymer with different additives were prepared by addition of one weight per cent of various photosensitizers to the copolymer and milling at 120°C. until homogeneous compositions were obtained. The blends were pressed into plaques five inches in diameter and ten mils thick at mold temperatures of 120°C. to 150°C. One inch square samples were cut from these plaques and irradiated for various periods of time by exposure to the predominantly continuum visible light radiation emanating from a 50 kilowatt swirl-flow plasma arc radiation source employing argon as the gaseous medium. The samples were irradiated at a distance of one foot from the arc. After irradiation the films were extracted with hot ethylbenzene to constant weight to determine the extent of cure that had been achieved. The cured copolymer was insoluble whereas the uncured copolymer was soluble in the hot solvent. It was found that about 90 per cent cure was achieved in about one minute. This fast rate of curing on exposure to predominantly continuum visible light radiation was completely unexpected and un-	35
40	obvious. Samples cured using a 550 watt mercury lamp required about 20 minutes of exposure to obtain cures similar to those obtained in 20 seconds with the light radiation from the swirl-flow plasma arc radiation source. The results are tabulated below:	40
45		45

Radiation Source	SFPA				Mercury Lamp				
Exposure Time	Seconds				Minutes				
	5	10	20	60	2	5	20	60	120
Additive	Per Cent Insoluble Copolymer								
p-Methoxybenzophenone	77	86	88	96	48	72	91	93	92
3-Chloroxanthone	32	63	64	89	25	47	76	86	—
Benzophenone	58	66	85	89	42	61	85	87	92
None	1	8	34	54	25	32	34	62	

SFPA = Swirl-flow plasma arc radiation source

Example 2

A copolymer of 98.9 mole per cent ethylene and 1.1 mole per cent bicyclo[2.2.1]-hept-2.5-diene was produced by polymerizing a mixture of said monomers in a conventional stirred reactor at a temperature of about 200°C. to 210°C. and a pressure of about 16,500 psi. The catalyst used was 216 molar ppm of azo-bis-isobutyronitrile in acetone solution. The copolymer had a melt index of 5.3 dgm./min. and a density of 0.9281 g./cc.

Blends of the copolymer were produced with different photosensitizer additives, in the manner described in Example 1, and 100 mil thick film plaques were produced for irradiation. The photosensitizer was present at a concentration of one weight per cent. The films were irradiated at a distance of one foot from the same arc and the extent of crosslinking was determined by measuring the amount of insoluble copolymer remaining after extraction with hot ethylbenzene. For comparison purposes the same films were irradiated with a 550 watt mercury lamp. The rapid curing rate of this thick a film upon exposure to the radiation from the swirl-flow plasma arc radiation source was a completely unexpected and unobvious finding. The data show that increasing the concentration of the additive increases the amount of crosslinking that occurs in the same period of exposure to radiation. The results are tabulated below:

Radiation Source	SFPA				Mercury lamp				
Exposure Time	Seconds				Minutes				
	5	10	20	60	2	5	20	60	300
Additive	Per Cent Insoluble Copolymer								
3-Chloroxanthone	31	36	44	70	30	42	56	63	65
Chlorononylxanthone	18	33	63	69	21	39	51	64	63
p-Methoxybenzo-phenone	21	33	40	55	21	29	44	47	53
p-Methoxyaceto-phenone (a)	26	32	47	65					
„	19	21	30	51	20	—	56	64	—
„ (b)	15	19	31	36					
Propiophenone	2	5	12	30					
„ (a)	21	19	41	52					
None	10	11	19	24					

SFPA = Swirl-flow plasma arc radiation source

a — at 5 weight per cent concentration

b — at 0.5 weight per cent concentration

Example 3

An ethylene/5-ethylidenebicyclo[2.2.1]hept-2-ene copolymer was produced by polymerizing a mixture of ethylene and one mole per cent 5-ethylidenebicyclo[2.2.1]hept-2-ene at a pressure of 23,500 psi and a temperature of 195°C. The catalyst was dilauryl peroxide. The copolymer had a density of 0.9284 g./cc.

The copolymer was blended with several different photosensitizer additives and molded into 10 mils plaques by a procedure similar to that described in Example 1. Portions of each plaque were irradiated with an argon swirl-flow plasma arc radiation source at a distance of one foot from the arc. Even in the absence of a photosensitizer the copolymer cured to the extent of 15 per cent in sixty seconds. The fast cure rate obtained was unexpected and completely unobvious. The results are set forth below:

Exposure time, sec.	Conc. Wt. %	Per Cent Insoluble Copolymer			
		5	10	20	60
<u>Additive</u>					
3-Chloroxanthone	1	40	44	68	74
p-Methoxybenzophenone	5	18	39	46	70
„	1	24	32	44	64
p-Bromobenzophenone	1	22	25	50	42
None		4	3	7	15

Example 4

Ten mil thick films were produced using the ethylene/bicyclo[2.2.1]hept-2,5-diene copolymer of Example 2 blended with one weight per cent of p-methoxyacetophenone. Three of these films were stacked on top of each other and separate stacks were irradiated with light radiation from an argon 50 kilowatt swirl-flow plasma arc radiation source and from a 550 watt medium pressure mercury lamp, both at a distance of one foot. All three layers of films in the stack exposed to the swirl-flow plasma arc radiation source unexpectedly showed a greater cure after sixty seconds than the respective layers in the stack exposed to the mercury arc for sixty minutes. This experiment also established that the process of this instant invention could be used to cure multiple layers at the same time. The results are set forth below:

Radiation Source	Exposure Time	Per Cent Insoluble Copolymer		
		Top Film	Middle Film	Bottom Film
SFPA	60 seconds	67	54	48
Mercury lamp	60 minutes	41	24	14

SFPA=Swirl-flow plasma arc radiation source

Example 5

A commercially available silicone rubber gumstock having an average molecular weight of about 400,000 containing about 64.5 per cent of a solid dimethylsiloxane (98.8)/methyl vinyl siloxane (0.2) copolymer, about 9.5 per cent of a liquid low molecular weight ethoxy end-blocked poly(dimethylsiloxane) and 26 per cent silica filler was blended on a roll mill with different additives until homogeneous mixtures were obtained. The homogeneous blends were cold pressed into 100 mil sheets which were irradiated at a distance of two feet with the swirl-flow plasma arc radiation source described in Example 1. The results set forth below show the unexpected rapid curing achieved by the process of this invention even on polymeric compositions containing inert inorganic fillers; they also show that rapid, uniform curing can be obtained through thick sheets. Crosslinking was not observed on the silicone rubber when the additive was not added thereto.

Additive	Conc. Wt. %	Exposure Time Seconds	Hardness (Shore A Units)	Elongation %	Tensile psi	Set at Break %
None		300	***	***	<100	***
Silanic hydrogen crosslinker*	3.2	180	16	90	780	68
		300	17	200	833	47
Dichlorobenzoyl peroxide**	1.6	30	40	365	610	15
		60	47	700	610	6
		120	52	930	500	0
2,5-Dimethyl-2,5-di(t-butyl peroxy) hexane	0.64	60	26	840	1010	17
		120	30	1040	900	10
		180	33	1175	770	6
Benzophenone	0.64	40	15	60	625	70
		60	23	90	700	40
		120	34	940	975	12
Silanic hydrogen crosslinker*	3.2	30	18	75	500	30
Benzophenone	0.64	60	20	200	725	27
		120	20	400	750	19
Dichlorobenzoyl peroxide **	1.6	20	45	870	630	4
Benzophenone	0.64	30	50	1215	610	1
		60	52	1250	620	1
		90	48	1140	500	1
Benzophenone	0.64	30	18	130	915	60
2,5-Dimethyl-2,5-di(t-butyl peroxy)hexane	0.64	60	29	520	1000	24
		90	35	700	850	12
		120	26	630	850	13

* Poly(methyl hydrogen siloxane)end-blocked with trimethyl silyl groups; viscosity 30 csp. at 25°C.

** As a 50 per cent paste in a low molecular weight poly(dimethylsiloxane)

*** Too low to measure.

Example 6

A mixture of 490 grams of a commercially available polycaprolactone diol having an average molecular weight of about 2,000 of the structural formula:

$\text{HO}[(\text{CH}_2)_5\text{COO}]_n\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2[\text{OOC}(\text{CH}_2)_5]_m\text{OH}$ and six grams of 2-ethoxyethanol was heated to 80°C. in a polymerization reactor. Over a 35 minute period 320.3 grams of di(2-isocyanatoethyl)bicyclo[2.2.1]hept-5-en-2,3-dicarboxylate were added and then the mixture was stirred for another hour at 80°C. During the addition, an exotherm of 94°C. was reached. At the end of the hour, another six grams of 2-ethoxyethanol were added and the mixture was stirred for 30 minutes at 80°C. The urethane polymer had an inherent viscosity of 0.42 as determined at 30°C. using a 0.5 per cent solution in m-cresol.

A 50 per cent solution of the above urethane polymer, containing one weight per cent of p-methoxybenzophenone, based on the polymer, was prepared in methyl ethyl ketone. Films of this solution were cast on glass plates and the solvent was evaporated to leave a highly viscous fluid film about 10 mils thick. The film was irradiated at a distance of one foot from a 50 kilowatt argon swirl-flow plasma arc radiation source to produce a self-sustaining plastic film within 30 seconds. To achieve about the same degree of cure with a 550 watt medium-pressure mercury arc required an irradiation time of 25 minutes. Irradiated to the same degree of insolubilization, the film irradiated with the swirl flow plasma arc radiation source had better physical properties.

Radiation Source	Exposure Time	Per Cent Insoluble Copolymer	Stiffness psi	Tensile psi	Elongation %
SFPA	30 seconds	88	605	231	61
Mercury lamp	25 minutes	90	377	182	98

Example 7

A blend of a commercially available polyethylene having a melt index of 0.8 dgm./minute and a density of 0.9613 g./cc. with one weight per cent 3-chloroxanthone was prepared and 10 mil thick plaques were produced by pressure molding at 190°C. The plaques were irradiated at a distance of one foot from a 50 kilowatt argon swirl-flow plasma arc radiation source for different exposure times and extracted with boiling ethylbenzene to constant weight to determine the extent of gel or crosslinking. Irradiation for five seconds resulted in 12 per cent cure, for ten seconds in 15 per cent cure, for 20 seconds in 24 per cent cure, and for 60 seconds in 50 per cent cure.

Example 8

A mixture of 100 grams of cellulose acetate (38.3 per cent acetyl content) and one liter of methyl ethyl ketone was heated to 60°C. and two drops of dibutyl tin dilaurate were added. Over a 55 minute period, 100 grams of bicyclo[2.2.1]hept-5-en-2-yl-methylisocyanate were added and stirring was continued for 21 hours at 60°C. Benzene was added to the cooled solution to precipitate the cellulose acetate bicyclo[2.2.1]hept-5-en-2-ylmethylcarbamate polymer, which was filtered, washed with isopropanol and dried. Elemental analysis established that all the available hydroxyl groups had reacted with the isocyanate and formed carbamyl groups.

The cellulose acetate-5-norbornen-2-ylmethylcarbamate copolymer was used to produce films about 10 mils thick. The films were irradiated at a distance of two feet from a 50 kilowatt argon swirl-flow plasma arc radiation source, under a blanket of nitrogen. Portions of the film were removed at different times and extracted with hot acetone to constant weight to determine the extent of crosslinking. After 30 seconds exposure the polymer showed 21 per cent crosslinking, after 60 seconds the polymer was crosslinked to the extent of about 32 per cent, and after 120 seconds crosslinking had proceeded to the extent of 77 per cent.

A second series of irradiations was carried out using films produced from a blend of the same copolymer containing one weight per cent xanthone. Irradiation for five seconds resulted in 47 per cent crosslinking, after 30 seconds the polymer was crosslinked to the extent of about 75 per cent, and after 60 seconds crosslinking had reached a maximum of 88 per cent.

Example 9

The same copolymer described in Example 1 was used to produce films 10 mils thick which were then irradiated as described in Example 8. The extent of crosslinking achieved after exposure is set forth below:

5	Exposure Time, Seconds	Crosslinking, %	5
	7	26	
	15	33	
	33	39	
	60	48	
10	150	60	10
	300	74	

Example 10

15 A solution of 54.8 grams of 4,5 di-(chlorocarbonyl)-bicyclo[2.2.1]hept-2-ene in 100 ml. of toluene was slowly added, while stirring, to 100.7 grams of polyethylene glycol having an average molecular weight of about 400 that was dissolved in 59.3 grams of pyridine and 250 ml. of toluene. The reaction flask was purged with nitrogen during the addition. An exothermic reaction occurred with the temperature rising to 80°C. The viscous solution was refluxed at 110°C. for one hour and poured into a solution of four liters of water and one liter of chloroform. The mixture was 20 thoroughly shaken, the chloroform layer was removed and dried over anhydrous magnesium sulfate, and the solvents distilled off under reduced pressure. The viscous polyester was vacuum distilled at 100°C. and 0.3 mm. mercury pressure for 1.5 hours to yield 111.9 grams of the brownish, viscous, tacky polyester having the repeating unit.

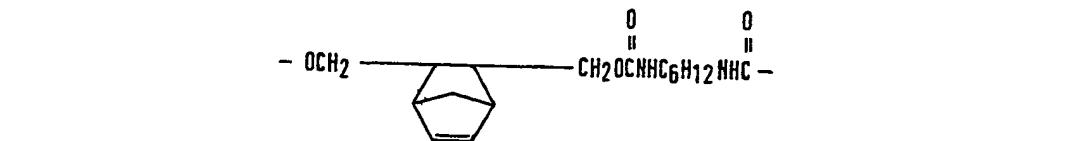


A film was cast from the polyester and irradiated for ten minutes at a distance of four feet from the arc of a 50 kilowatt argon swirl-flow plasma arc radiation source. The polyester crosslinked to a rubbery film that was 74 per cent insoluble in hot benzene, the polyester was completely soluble in the same solvent prior to irradiation.

30 A period of 2.2 hours (132 minutes) is necessary to achieve about the same amount of crosslinking with a 550 watt high pressure mercury lamp positioned only 16 inches from the film.

Example 11

35 A polymerization reactor was equipped with a stirrer, nitrogen purge, thermometer and addition tube and immersed in an oil bath. About 30.8 grams of 5,6-di-(hydroxymethyl)bicyclo[2.2.1]hept-2-ene was placed in the reactor, purged with nitrogen, and heated to 125°C. A total of 33.6 grams of 1,6-hexamethylene-diisocyanate was slowly added while raising the temperature to 170°C. so that the reaction reached this temperature at about the same time that the addition of the diisocyanate was 40 completed. The urethane polymer was very viscous and fibers could be easily pulled from the molten mass. The polymer had repeating units of the formula:



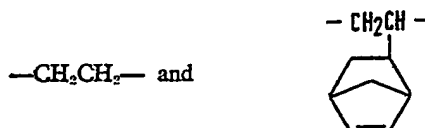
It was soluble in a 1:1 chloroform-methanol solution and films were cast from solutions thereof. Films and plaques were also produced by compression molding. The urethane polymer had a tensile modulus of 213,000 psi, a tensile strength of 9,400 psi and an elongation of 6.3 per cent. The cast film, 10 mils thick, was irradiated with the light radiation from a 50 kilowatt swirl-flow plasma arc radiation source at a distance of one foot for 30 seconds and it was crosslinked to the extent

of 48 per cent insolubilization. The same polymer required over 20 hours of exposure to ultraviolet radiation from a 100 watt mercury lamp to achieve about the same degree of crosslinking.

Example 12

5 Ethylene/5-vinylbicyclo[2.2.1]hept-2-ene copolymer was produced by polymerizing a mixture of ethylene and 0.5 mole per cent 5-vinylbicyclo[2.2.1]hept-2-ene at a temperature of about 200°C. and a pressure of about 25,000 psi. The catalyst was dilauryl peroxide. A blend of four runs of copolymers having melt indices of 164 dgm./min. and a density of about 0.93 g./cc. was used in the following treatment.

10 The copolymers contained polymerized units of the formulae:



in the molecule and they were soluble in boiling ethylbenzene.

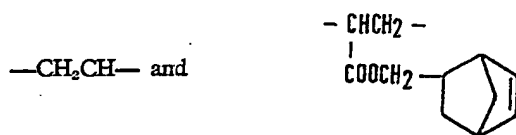
15 Films were molded to a thickness of 10 mils and then irradiated with the light radiation from a 50 kilowatt argon swirl-flow plasma arc radiation source at a distance of one foot from the light source.

20 The same copolymer mixture was blended with one weight per cent p-methoxybenzophenone and films thereof were similarly exposed to the swirl-flow plasma arc radiation source. The results, tabulated below show the unexpected advantages accruing from the use of selected photosensitizing agents; the amount of crosslinking was two and one-half times as great. Crosslinking was determined by measuring the amount of insoluble polymer remaining after repeated extractions with boiling ethylbenzene.

Exposure Time. seconds	Per Cent Insolubles	
	Without Additive	With 1 wt. % p- methoxybenzophenone
5	5	11.4
10	8.9	23.4
20	12.6	58.9
60	20.6	—

Example 13

25 An ethylene/bicyclo[2.2.1]hept-5-en-2-ylmethyl acrylate copolymer was produced by polymerizing a mixture of ethylene and 0.05 mole per cent bicyclo[2.2.1]hept-5-en-2-ylmethyl acrylate at about 205°C. and a pressure of about 19,000 psi. The catalyst was an isopropanol solution of azobis(isobutyronitrile). The copolymer had a density of 0.9233 g./cc. The copolymer contained polymerized units of the formulae:



in the molecule. It had a melt index of about 1.5 dgm./minute and it was soluble in boiling ethylbenzene.

35 Films, 10 mils thick, were irradiated as described in Example 12. In the absence of any added photosensitizer the copolymer crosslinked to the extent of five per cent after a 60 second exposure to the argon swirl-flow plasma arc radiation source. Films produced from a blend of the copolymer with one weight per cent

3-chloroxanthone showed more than five per cent crosslinking after less than three seconds exposure to this irradiation source and over 60 per cent crosslinking after a 35 second exposure. The results are tabulated below:

Exposure Time seconds	Per Cent Insolubles	
	Without Additive	With 1 wt. % 3-Chloroxanthone
5	0.9	12.5
10	0.1	28.2
20	3.1	46.7
60	6.9	61.2

5

Example 14

5

A series of polymers was produced and used to impregnate paper to improve the wet strength characteristics of the paper. The polymers were produced as follows:

10

Polymer A — The urethane polymer described in Example 18.

Polymer B — A urethane polymer produced as described in Example 6 except that 7.5 grams of 2-ethoxyethanol were used in each addition. The urethane polymer had an inherent viscosity of 0.33 as determined at 30°C. using a 0.5 per cent solution in m-cresol.

15

Polymer C — Using the procedure described infra for Polymer D, 128.3 grams of the propylene oxide adduct of glycerol having an average molecular weight of about 1,000 and an hydroxyl number of about 168 were reacted with about 88 grams of bis(2-isocyanatoethyl)bicyclo[2.2.1]hept-5-en-2,3-dicarboxylate and then with 38.5 grams of butoxydiethylene glycol. The urethane polymer weighed 242.7 grams and it had a reduced viscosity of 0.102 as determined at 30°C. using a 0.5 per cent solution in benzene.

20

Polymer D — A glass polymerization vessel was charged with 200 ml. of benzene and 128.3 grams of castor oil and two drops of dibutyltin dilaurate were dissolved therein. Over a ten minute period 80 grams of bis(2-isocyanatoethyl)bicyclo[2.2.1]hept-5-en-2,3-dicarboxylate were added; the temperature rose exothermically and about 40 minutes after this addition was it had risen to a maximum of 39°C. The viscous solution was stirred another 20 minutes, 38.5 grams of butoxydiethylene glycol was added thereto, stirred and then left standing overnight at room temperature. The following day the benzene was removed by vacuum distillation. The urethane polymer weighed 249.1 grams and it had a reduced viscosity of 0.103 as determined at 30°C. using a 0.5 per cent solution in benzene.

25

Polymer E — Using the procedure described for polymer D, 100 grams of the reaction product of 1 part of the propylene oxide adduct of glycerol having an average molecular weight of about 260 and 2 parts of epsilon caprolactone (said reaction product having an average molecular weight of about 800) were reacted with about 88 grams of bis(2-isocyanatoethyl) bicyclo[2.2.1]hept-5-en-2,3-dicarboxylate and then with 32.3 grams of butanol. The urethane polymer weighed 199.5 grams and it had a reduced viscosity of 0.086 as determined at 30°C. using a 0.5 per cent solution in benzene.

30

Polymer F — The polyester described in Example 29.

35

The polymers were used to prepare acetone solutions containing 10 weight per cent of the polymer, one weight per cent dichlorobenzoyl peroxide and one weight per cent benzophenone. Samples of paper were immersed in the acetone solutions and air dried; the dried papers had a polymer retention of 20 weight per cent on the weight of the paper. The impregnated paper samples were exposed to a 50 kilowatt argon swirl-flow plasma arc radiation source for 90 seconds at a distance of two feet. Tensile strengths were measured on the untreated paper, the treated paper prior to irradiation, and the treated paper after irradiation. The tensile strengths were measured on irradiated and unirradiated dry paper samples and wet paper samples that had been immersed in water at 25°C. for 15 minutes. The results are set forth below:

40

45

50

40

45

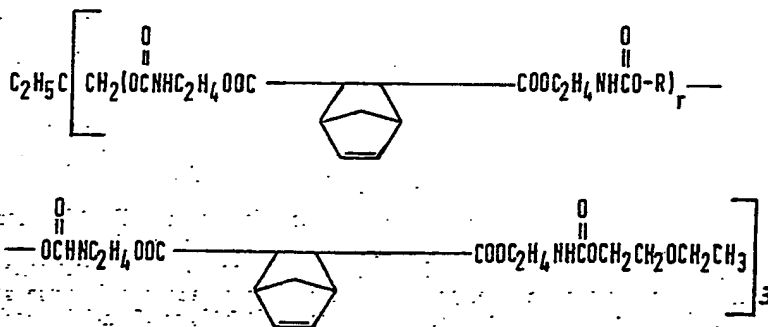
50

Polymer	Tensile strength, psi*			
	Dry		Wet	
	Not Irrad.	Irrad.	Not Irrad.	Irrad.
None, Control	14.5	—	1.2	—
A	10.5	17.5	1.1	6.5
B	11.5	22.0	1.3	7.9
C	9.5	15.0	1.0	4.5
D	11.0	16.0	1.6	6.7
E	12.0	19.5	1.2	7.2
F	16.0	27.0	2.4	9.4

*Reported in pounds/two inch strip.

Example 15

There were charged to a reaction vessel 245 grams of a polycaprolactone diol having an average molecular weight of about 530 and 45.1 grams of 2-ethoxyethanol and the mixture was heated to 80°C. While stirring, 320.3 grams of di(2-isocyanatoethyl)bicyclo[2.2.1]hept-5-en-2,3-dicarboxylate was added all at once. The temperature rose exothermically to 115°C. and then declined. The reaction mixture was stirred at 80°C. for another 1.5 hours and then 22.8 grams of trimethylolpropane was added in one portion. After stirring for 45 minutes at 100°C. the viscous urethane polymer was cooled; the yield was 620 grams. The polymer was a tacky gum that had an inherent viscosity of 0.145 as determined from a 0.5 weight per cent solution in m-cresol at 30°C.; it can be represented by the formula:



in which R is



wherein m and n have an average sum total of about 3.5 and r is an integer.

The polymer was used to produce films 10 mils thick, that were irradiated at a distance of one foot with the light radiation from an argon swirl-flow plasma arc radiation source. In addition, blends of the polymer with one weight per cent of the photosensitizers p-methoxyacetophenone and 3-chloroxanthone were also produced and 10 mils films thereof were similarly irradiated. The films crosslinked and cured to solid hard films after exposure for a matter of seconds. In comparison, a minimum of 25 minutes was necessary to cure the polymers to a hard film when the same compositions were exposed to a 550 watt mercury arc at a distance of one foot. The results are tabulated below:

Photosensitizer	Cure time to hard film	
	SFPA, seconds	Hg arc, minutes
None	>30	55
p-Methoxyacetophenone	10	25
3-Chloroxanthone	5	55

SFPA-Argon swirl-flow plasma arc radiation source.

Example 16

In a manner similar to that described in Example 15, a urethane polymer was produced by the reaction of 300 grams of polyethylene glycol having an average molecular weight of about 600, 45.1 grams of 2-ethoxyethanol, 320.3 grams of di(2-isocyanatoethyl) bicyclo[2.2.1]hept-5-en-2,3-dicarboxylate and 22.8 grams of trimethylolpropane. There was recovered 653 grams of a tacky urethane polymer having an inherent viscosity of 0.23 as determined from a 0.5 per cent solution in m-cresol at 30°C. In this polymer the R moiety is represented in the formula shown in Example 15 by the group of the formula $-(CH_2CH_2O)_xCH_2CH_2-$ wherein x has an average value of about 12.

The polymer was used to produce films, by the procedure in Example 15, and these were crosslinked. It was found that exposure to the argon swirl-flow plasma arc radiation source produced a hard film in a matter of seconds as compared to a much longer period of time required with the mercury arc. The results are tabulated below:

Photosensitizer	Cure time to hard film	
	SFPA, seconds	Hg arc, minutes
None	>30*	40
p-Methoxyacetophenone	10	15
3-Chloroxanthone	10	20

*No cure observed after 30 seconds irradiation.

Example 17

In a manner similar to that described in Example 15, a urethane polymer was produced by the reaction of 503.5 grams of polypropylene glycol having an average molecular weight of about 1025, 45.1 grams of 2-ethoxyethanol, 320.3 grams of di(2-isocyanatoethyl)bicyclo[2.2.1]hept-5-en-2,3-dicarboxylate and 22.8 grams of trimethylolpropane. Two drops of dibutyltin dilaurate catalyst were added in the first step of the reaction. There was produced 885.2 grams of a tacky urethane polymer having an inherent viscosity of 0.196 as determined from a 0.5 per cent solution in m-cresol at 30°C. In this polymer the R moiety in the formula shown in Example 15 is represented by the group $-(CH_2CHO)_yCH_2CH-$ wherein y has an average value



of about 16.5.

Films, 10 mils thick, were produced and irradiated as described in Example 15. The argon swirl-flow plasma arc radiation source was much more effective and successfully cured the surface of the film containing the photosensitizers in seconds, whereas the mercury arc failed to cure the polymer in the absence of a photosensitizer or when 3-chloroxanthone was used as the photosensitizer. The polymer blends with the photosensitizers cure to hard films upon continued irradiation. The results are tabulated below:

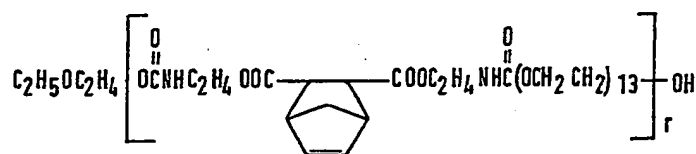
Photosensitizer	Cure time to hard film	
	SFPA, seconds	Hg arc, minutes
None	30	None after 60 min.
p-Methoxyacetophenone	10**	45*
3-Chloroxanthone	10**	None after 60 min.

* No cure observed after 30 seconds irradiation

** Surface cure only

Example 18

A mixture of 600 grams of polyethylene glycol having an average molecular weight of about 600 and 7.5 grams of 2-ethoxyethanol was reacted with 320.3 grams of di(2-isocyanatoethyl) bicyclo[2.2.1]hept-5-en-2,3-dicarboxylate as described in Example 15. The exotherm temperature reached was about 129°C. After stirring for one hour at 80°C., another 7.5 grams of 2-ethoxyethanol were added and stirring was continued for 30 minutes at 80°C. The yield was 899.6 grams of a tacky urethane polymer having an inherent viscosity of 0.51 as determined from a 0.5 per cent solution in m-cresol at 30°C. The polymer can be represented by the general formula set forth in which r is an integer.



Films, 10 mils thick, were produced from the tacky polymer and irradiated as described in Example 15. The argon swirl-flow plasma arc radiation source was much more effective, with or without added photosensitizers, than was the mercury arc in curing and crosslinking the polymer. The results are tabulated below:

Photosensitizer	Cure time to hard film	
	SFPA, seconds	Hg arc, minutes
None	30	30
p-Methoxyacetophenone	5—10	15
3-Chlorosanthone	10	15

Example 19

A mixture of 4,100 grams of bicyclo[2.2.1]hept-5-en-2,3-dicarboxylic acid anhydride, 5,400 grams of 2,2-dimethyl-3-hydroxypropyl 2,2-dimethyl-3-hydroxypropionate and 240 grams of pentaerythritol was polymerized by heating at 200°C. until the polyester had an acid number of 10.4. The polyester had a reduced viscosity of 0.072 at 30°C. using a 0.2 per cent benzene solution.

The polyester was used to produce 100 percent solids coating compositions by mixing 70 parts of the liquid polyester with 30 parts of various acrylate monomers, by weight. To portions of each of the coating compositions produced there was also added one weight per cent of various photosensitizers. The 100 per cent solids coating compositions were coated on glass and exposed to the light radiation from an argon swirl-flow plasma arc radiation source at a distance of one foot from the arc. The compositions crosslinked and cured to films with a ten second exposure to the light radiation. In the table that follows, the diacrylate monomer used is shown in the first column and in the right hand columns the properties of the irradiated films produced with the compositions containing the different photosensitizers is indicated.

Film Property

Acrylate Monomer	Photosensitizer Present			
	None	A	B	C D
Bicyclo[2.2.1]hept-5-en-2-ylmethyl acrylate	Gel	Gel	Gel	Gel —
Neopentyl glycol diacrylate	Hard	Hard**	Hard	Soft —
Tetramethylene glycol diacrylate	—	Gel	Gel	*** —
2-Methyl-2-ethyl-1,3-propanediol diacrylate	Hard	Hard	Hard	Hard**
Pentamethyleneglycol diacrylate	Soft	Hard	Hard	— Hard
Polyethylene glycol *diacrylate	Soft	Soft	Soft	— Soft
2-Butoxyethylacrylate ****	***	—	Soft	— Soft

* Average molecular weight of about 200

** After irradiation for five seconds

*** Surface cured

**** Composition contained 75% polyester and 25% of the acrylate monomer.

A — 3-Chloroxanthone

B — p-Methoxybenzophenone

C — p-Methoxyacetophenone

D — Benzophenone

Example 20

The same polyester described in Example 19 was mixed with various unsaturated monomers to produce coating compositions containing 70 weight per cent polyester and 30 weight per cent monomer. The liquid solutions were cast onto glass slides to a thickness of about 5 mils and irradiated for one and two minutes with the light radiation from a 50 kilowatt argon swirl-flow plasma arc radiation source at a distance of two feet from the arc. The liquid coating compositions cured to solid, self-supporting films that could be stripped off the glass surface. The extent of crosslinking or cure was determined by extraction with boiling acetone to constant weight and calculation of the per cent insoluble polymer remaining. The results are tabulated below:

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Exposure time, min. Monomer	Per Cent Insoluble	
	1	2
2-Butoxyethyl acrylate	57.6	75.1
2-Phenoxyethyl acrylate	7.7	26.6
2-Ethylhexyl acrylate	43.4	71.9
2-Phenylethyl acrylate	30.4	48.9
Furfuryl acrylate	11.8	23.4
Bicyclo[2.2.1]hept-5-en-2-ylmethyl acrylate	35.0	51.8
Dicyclopentenyl acrylate	50.3	66.0
2-Dicyclopentenoxylethyl acrylate	13.9	47.2
6-Dicyclopentenoxylhexyl acrylate	11.3	33.3
Bicyclo[2.2.1]hept-5-en-2-ylmethyl methacrylate	2.3	42.7
Butanediol diacrylate	72.5	75.8
Pentanediol diacrylate	62.9	73.3
Neopentyl diacrylate	63.4	73.3
2-Methyl-2-ethylpropanediol diacrylate	65.5	73.0
Polyethyleneglycol (M.W. 200)dimethacrylate)	43.6	48.5
Styrene	8.3	23.5

Example 21

5 A commercially available copolymer of ethyl acrylate (60)/methyl methacrylate (39)/acrylic acid (1) was blended with acrylate monomers to produce two different 100 per cent solids coating compositions. The liquid coating compositions were used to cast five mil liquid films on a glass surface and the coatings were irradiated for two minutes, at a distance of two feet, with the light radiation from an argon swirl-flow plasma arc radiation source. The coatings crosslinked and cured to solid, self-supporting films that could be stripped off the glass surface. The extent of crosslinking or cure was determined by extraction with boiling benzene to constant weight and calculating the per cent of gelled or insoluble polymer remaining. The two compositions prepared and the per cent insoluble polymer after irradiation are set forth below:

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Composition	Insoluble, %	
Acrylate copolymer	30%	47.7
Dicyclopentadienyl acrylate	35%	
2-Butoxyethyl acrylate	25%	
Polyethyleneglycol (M.W. 200) acrylate	10%	53.3
Acrylate copolymer	30%	
Dicyclopentadienyl acrylate	35%	
2-Butoxyethyl acrylate	25%	
Butanediol diacrylate	10%	

Example 22

A 100 per cent solids coating composition was produced containing 30 per cent of a lauryl methacrylate (95)/bicyclo[2.2.1]hept-5-en-2-ylmethyl acrylate (5) copolymer, 35 per cent dicyclopentadienyl acrylate, 25 per cent 2-butoxyethyl acrylate and 10 per cent polyethylene glycol (M.W. 200) diacrylate. Films thereof cast on glass, irradiated as described in Example 22, crosslinked to the extent that 75.7 per cent of the irradiated polymer was insoluble in boiling benzene.

The lauryl methacrylate/bicyclo[2.2.1]hept-5-en-2-ylmethylacrylate copolymer was produced by charging 12 grams of bicyclo[2.2.1]hept-5-en-2-ylmethyl acrylate, 228 grams of lauryl methacrylate, 120 grams of benzene, 120 grams of toluene and 3.2 grams of t-butyl peroxyphthalate to a Pyrex pressure reactor (Pyrex is a Registered Trade Mark). The polymerization was carried out at 40°C. for about 66.5 hours. The copolymer was precipitated by pouring the reaction mixture into methanol, it was washed in methanol and vacuum dried at 50°C. The yield was 93.3 per cent and the resin was completely soluble in cyclohexane.

Example 23

The same polyester described in Example 19 was blended with varying amounts of neopentylglycol diacrylate and the resulting liquid coating compositions were cast into 10 mil liquid films on a glass surface. The liquid films were irradiated for various times at a distance of two feet under a 50 kilowatt argon swirl-flow plasma arc radiation source. In one series the liquid coating compositions contained no photosensitizer and in the other series the compositions were sensitized with one weight per cent benzil as the photosensitizer. The series included radiation of the monomer alone, without the presence of the polyester. In all instances, solid, hard films were produced after irradiation. The extent of curing or crosslinked polymer produced after the irradiation was determined on the films by extraction of the irradiated polymer with boiling benzene to constant weight to determine the amount of insoluble crosslinked polymer remaining. The data shows that not only is this irradiation process useful for crosslinking polymer compositions but it is also useful for rapidly polymerizing monomers to solid polymeric compositions.

% Neopentylglycol Diacrylate	% Insoluble at Various Times (Seconds)							
	Unsensitized				Sensitized			
	15	30	60	120	15	30	60	120
10	31	38	—	47	24	41	46	52
20	49	48	54	58	—	47	52	67
25	48	57	64	56	39	41	54	56
35	61	64	70	75	60	63	68	71
40	62	64	73	77	63	64	71	77
50	58	68	74	83	65	69	87	81
60	61	65	73	93	66	76	89	89
80	0	0	75	93	32	74	94	96
100	0	0	25	98	12	67	82	99

Example 24

5 The polyester described in Example 19 was blended with varying amounts of 2-butoxyethyl acrylate and the liquid compositions were cast on glass surfaces to form 10 mils thick films. The liquid films were irradiated at a distance of two feet with a 50 kilowatt argon swirl-flow plasma arc radiation source. In one series the 100 per cent solids coating compositions contained no photosensitizer and in the other series the compositions were sensitized with one weight per cent benzil as the photosensitizer. In addition, the monomer alone was subjected to irradiation. 10 The extent of crosslinking or crosslinked polymer produced in the polymerization was determined on the solid films in the manner described in Example 23. The data is set forth below:

% Butyl Cellosolve Acrylate (Cellosolve is a Registered trade Mark)	% Insoluble at Various Times (Seconds)							
	Unsensitized				Sensitized			
	15	30	60	120	15	30	60	120
10	21	35	37	22	30	23	24	49
20	29	35	42	46	32	46	57	64
25	22	36	39	51	26	—	59	61
30	23	35	43	60	43	57	—	71
35	30	35	46	60	26	54	54	74
40	27	32	50	56	30	59	58	66
50	17	34	62	56	32	87	82	68
60	18	40	64	68	17	40	58	65
80	31	67	68	61	23	45	60	72
100	0	0	—	35	0	21	25	44

Example 25

A 100 per cent solids coating composition was produced containing 70 weight per cent of the polyester of Example 19 and 30 weight per cent of neopentyl glycol diacrylate. The composition was blended with various photosensitizers and initiators, as a concentration of one weight per cent each, and the liquid sensitized solutions were cast as 10 mils thick films on glass plates. The liquid films were irradiated for 20 seconds, at a distance of one foot, under a 50 kilowatt argon swirl-flow plasma arc radiation source. After exposure the films were hard and solid; they were extracted to constant weight with boiling benzene and the amount of crosslinked polymer formed was determined by the amount of insoluble polymer remaining. The results are tabulated below:

Photosensitizer	Insoluble Polymer, %
Benzophenone	74
Benzophenone + benzoyl peroxide	68
Benzophenone + dichlorobenzoyl peroxide	73
p-Methoxybenzophenone	70
p-Methoxybenzophenone plus benzoyl peroxide	73
p-Methoxybenzophenone plus dichlorobenzoyl peroxide	75
Benzil	76
Benzil plus benzoyl peroxide	78
Benzoyl peroxide	79
Dichlorobenzoyl peroxide	77

Example 26

A series of compositions was produced and used to impregnate paper sheets to a weight pick-up of 20 percent. The impregnated papers were then irradiated and cured for 90 seconds at a distance of two feet from a 50 kilowatt argon swirl-flow plasma arc radiation source. The tensile strengths were measured on the cured and uncured samples in the dry state and in the wet state after a 15 minute immersion in water at 25°C. The contents of each composition and the properties of the control paper samples are set forth below.

Composition A was a 100 per cent solids coating composition containing 70 parts by weight of the polyester of bicyclo[2.2.1]hept-2-en-5,6-dicarboxylic acid anhydride and 3-hydroxyneopentyl 3-hydroxypivalate, 30 parts of 2-butoxyethyl acrylate, one part dichlorobenzoyl peroxide and one part benzophenone.

Composition B was a 100 per cent solids coating composition containing 50 parts of the same polyester used in Composition A, 45 parts of a 2-butoxyethyl acrylate, 5 parts of neopentyl glycol diacrylate, one part dichlorobenzoyl peroxide and one part benzophenone.

Composition C contained 95 parts of 2-butoxyethyl acrylate, 5 parts of neopentyl glycol diacrylate, one part of dichlorobenzoyl peroxide and one part of benzophenone.

Tensile strength, psi*

Composition	Dry		Wet	
	Not Irrad.	Irrad.	Not Irrad.	Irrad.
None, control	14.5		1.2	
A	14.5	28.0	2.8	9.4
B	15.5	25.0	1.7	9.0
C	13.5	12.0	1.2	4.2

*Reported in pounds/two inch strip

Example 27

5 A polyester was produced by reacting 4,100 parts of bicyclo[2.2.1]hept-2-en-5,6-dicarboxylic acid anhydride, 5,400 parts of 2,2-dimethyl-3-hydroxypropyl 2,2-dimethyl-3-hydroxypropionate and 240 parts of pentaerythritol at 200°C. until the solution had an acid number of 10.4. The reduced viscosity of the polyester was 0.072 as determined at 30°C. from a 0.2 per cent solution in benzene. About 70 parts by weight of the polyester, 17 parts of 2-butoxyethyl acrylate and 13 parts of neopentyl glycol diacrylate were mixed in a flask and about 3.2 parts of bis(2-isocyanatoethyl) 5-norbornene-2,3-dicarboxylate were slowly added in a dropwise manner while maintaining a temperature of about 80°C. The reaction mixture was stirred until infrared analysis had indicated that all of the isocyanate groups had reacted. A five mils thick film cast on a glass plate cured to a hard film on exposure to the light radiation from a swirl-flow plasma arc radiation source at a distance of two feet from the arc. The addition of various photosensitizers and pigments shortened the exposure time needed to cure the polymer compositions to hard films; these blends were exposed at a distance of one foot from the arc. The results are tabulated below:

Run	Additives	Time, sec.
a	None	20
b	Benzil, 1%	1
c	Benzophenone, 1%	1
d	Benzophenone, 1% Dichlorobenzyl peroxide, 1%	0.4
e	Benzil, 1% Dichlorobenzoyl peroxide, 1% Naphthol Red, 30% (Color Index 161685)	5
f	Benzophenone, 1% Dichlorobenzoyl peroxide, 1% Naphthol Red, 30%	5
g	Benzil, 1% Dichlorobenzoyl peroxide, 1% Titanium dioxide, 30%	5
h	Fluorenone, 1% Dichlorobenzoyl peroxide, 1% Titanium dioxide, 30%	3

Example 28

20 A series of 100 per cent solids coating compositions was prepared containing 40 weight per cent of 2-butoxyethyl acrylate and 60 weight per cent of a norbornene-containing urethane polymer. In addition, blends of the coating compositions with 1 weight per cent of various photosensitizers were prepared. The liquid compositions were cast on glass plate to produce liquid films of 5 mils thick that were irradiated for various times at a distance of two feet from the arc with a 50 kilowatt swirl-flow plasma arc radiation source. In all instances crosslinking was achieved, as shown by the data tabulated below. The urethane polymers were as follows:

30 Polymer A — Polymer described in Example 15.
Polymer B — Polymer described in Example 16.
Polymer C — Polymer described in Example 18.
Polymer D — Polymer described in Example 17.

Urethane Polymer	Photosensitizer	Exposure time (sec.)		
		30	60	120
A	None	—	Surface Cure	Cured
	Propiophenone	—	"	"
	p-Methoxybenzophenone	—	"	Hard Film
	3-Chloroxanthone	Surface Cure	Hard Film	—
B	None	—	Surface cure	Cured
	Propiophenone	—	"	"
	p-Methoxybenzophenone	—	Hard Film	—
C	None	—	Surface cure	Cured
	Propiophenone	—	"	"
	p-Methoxybenzophenone	—	Cured	Hard Film
	3-Chloroxanthone	Surface Cure	Hard Film	—
D	None	None	None	Surface cure
	p-Methoxybenzophenone	"	Surface Cure	"

Example 29

Five moles of maleic anhydride were placed in a reaction flask equipped with a stirrer, thermometer, nitrogen purge tube, and a water condenser connected to a dry ice cold trap. The anhydride was melted by heating and at 125°C. to 150°C. 1,385 moles of bromine were slowly added. The mixture was cooled to 50°C., the water condenser and one mole of phthalic anhydride and 6.8 moles of ethylene glycol were added. The reaction mixture was stirred at 170°C. to 175°C. for about six hours while continuously bubbling nitrogen through the molten mass. The polyester had an acid number of about 50—60. At 150°C., 0.02 per cent hydroquinone inhibitor was added to the polyester and at 100°C. styrene was added to give a 30 per cent styrene solution. This 100 per cent solids coating composition was cast into films 20 mils thick and irradiated at a distance of two feet with the light radiation from a 50 kilowatt swirl-flow plasma arc radiation source. In addition, films produced from the same polyester blended with 0.1 per cent of various photosensitizers were similarly irradiated and crosslinked. In all instances the liquid coating composition cured to a solid film; the results are tabulated below.

Additive	Exposure time seconds	Film properties
None	120	Clear, rubbery brittle
Methylene blue (C.I. No. 52015)	120	Hard
Ethyl eosin (C.I. No. 45386)	90	Hard
Acridine orange (C.I. No. 46005)	90	Hard

Example 30

A commercially available polyester produced by the reaction of two moles of propylene glycol, one mole of maleic anhydride and one mole of dimethylterephthalate and having a Brookfield viscosity of 450,000 was used. Seventy parts of the polyester were dissolved in 30 parts of styrene to produce a 100 per cent solids coating composition. Portions of this composition were blended with 0.1 per cent of various photosensitizers. The solutions were used to cast liquid films 20 mils thick on glass plates. The films were irradiated at a distance of two feet with the light radiation from a 50 kilowatt argon swirl-flow plasma arc radiation source. In all instances the liquid coatings cured to solid films.

Additive	Exposure time Seconds	Film properties
None	120	Clear, rubbery brittle
Methylene blue	120	Hard
Ethyl eosin	20	Hard, brittle
Acridine orange	90	Hard, brittle

Example 31

Electrical conductors were produced with two different polyethylenes and two different metal conductors. Two copper wire conductors were produced using 14 CA coper wire, the first was insulated with a 30 mils covering of a polyethylene having a density of 0.918 g./cc. and a melt index of 0.108 dgm./min. (Conductor A) and the second was insulated with a polyethylene having a density of 0.945 g./cc. and a melt index of 0.2 dgm./minute (Conductor B). Two No. 4, 15 kilovolt sodium conductors were also prepared with 220 mils thick insulations using the same polyethylenes. The sodium conductor using the low density polymer is Conductor C and the sodium conductor using the high density polymer is Conductor D.

The insulated copper wires were irradiated by passing the wires continuously in a reflection chamber at a distance of about two to three inches from the arc and at a speed of 1.25 feet per minute through the light radiation from a 30 kilowatt argon swirl-flow plasma arc radiation source. The insulated wire became heated to about 95°C.

The insulated sodium cables were similarly irradiated except that they were passed through the light radiation zone four times at a speed of five feet per minute. The insulated cable heated to about 50° to 60°C.

The extent of crosslinking or per cent gel is the average of at least two determinations and was determined by stripping the insulation from the conductor and extracting with hot decalin to constant weight. The deformation under load was determined and the results are summarized below:

Conductor	Gel %	Deformation under load, %
A	66	
B	73	-1.5
C	16	
D	7.5	
Control, low density	0	melted
Control, high density	0	2.6

The copper wire conductors were also tested for flame resistance. The ends of the irradiated and unirradiated copper wire conductors were placed in a match flame. The insulation on the irradiated copper wire conductors glowed but it did not shrink or drip. The insulation on the control unirradiated copper wire conductors shrunk and dripped.

Example 32

The process was used to treat fabrics to improve the crease resistance. A 35/65 cotton/polyester and a cotton fabric were padded to 65 per cent wet pick up with the following solution in a conventional padding bath:

5	N-Methylolacrylamide	9 parts (by weight)	5
	Zinc nitrate solution	2 parts	
	Reaction product of a C ₁₅ linear secondary alcohol and 9 moles of ethylene oxide	0.01 part	
	Distilled water	89 parts	
10	p-Methoxybenzophenone	0.1 part	10

The padded fabric samples were mounted on conventional tenter frames and dried in a forced air oven at 200°F. for 3 minutes. Two methods were used for curing each sample.

Method A — The mounted fabric was irradiated at a distance of two feet with the light radiation from a 50 kilowatt argon swirl-flow plasma arc radiation source for 15 seconds and then placed in a forced air oven at 310°F. for 15 minutes.

Method B — The mounted fabric was given the same treatment but in reverse order.

Each fabric sample was then washed and dried in conventional laundry equipment using "Tide" (Tide is a Registered Trade Mark) detergent and then evaluated. The Monsanto Wrinkle Recovery test is AATCC Method No. 66—1659T; the Durable Press Ratings were determined by AATCC Method No. 124—1967T and the Tensile Strength by ASTM Method No. D1682—59T.

Fabric	Monsanto Wrinkle Recovery	Durable Press Rating	Tensile Strength psi
Cotton, untreated	160°		52
Method A	261°		28
Method B	263°		29
Cotton/polyester untreated		2.7	
Method A		3.8	
Method B		4.0	

Example 33

A 100 per cent solids coating composition was produced using 70 parts of the polyester of Example 19, 20 parts of 2-ethylhexyl acrylate and 10 parts of neopentylglycol diacrylate. The composition was blended with various photosensitizers and initiators and 3 mils thick coatings on steel panels were exposed to the light radiation from a 50 kilowatt argon swirl-flow plasma arc radiation source at a distance of two feet in a nitrogen atmosphere. It was found that adhesion was excellent in all instances and that the combination of additives gave a much better film coating.

Run	Additive	Exposure Time, sec.	Surface	Sward Hardness
a	None	40	W	
b	TEOA, 1%	40	W	
c	BP, 5%	30	W	
d	1% TEOA, 5% BP	20	S	8
e	" "	30	S	20
f	" "	40	S	32
g	" "	50	S	42
h	1% TEOA, 2% F	20	S	0
i	" "	30	S	4
j	" "	40	S	10
k	" "	50	S	12

TEOA — Triethanolamine
 BP — Benzophenone
 F — fluorenone
 W — wrinkled
 S — smooth

Example 34

A 100 per cent solids coating composition was produced using 70 parts of the polyester of Example 19, 22.5 parts of 2-ethylhexyl acrylate and 7.5 parts of neopentylglycol diacrylate. The composition was blended with various photosensitizers and initiators and 3 mils thick coatings on steel panels were exposed to radiation as described in Example 33. Adhesion was excellent except when benzoin was used as the photosensitizer; in all instances the surface was smooth.

Run	Additive	Exposure time, sec.	Sward Hardness
a	1% TEOA, 1% BE	20	2
b	" "	30	10
c	1% TEOA, 0.5% BEN	20	6
d	" "	30	10
e	1% TEOA, 5% BP	20	8
f	" "	30	20
g	" "	20*	6
h	1% TEOA, 0.5% BE	20*	6
i	" "	40*	10
j	" "	30	10

TEOA — triethanolamine
 BP — benzophenone
 BE — benzil
 BEN — benzoim
 * — radiated in air

Example 35

5 A 100 per cent solids coating composition was prepared by dissolving 30 g of poly(methyl methacrylate) having a reduced viscosity of 0.38 using a 0.5 weight per cent benzene solution in a mixture of 52.5 g of 2-butoxyethyl acrylate, 12.5 g of neopentyl glycol diacrylate, 5 g of 5-norbornene-2-ylmethyl 5-norbornene-2-carboxylate and 3 g of benzil. The coating was then applied to Bonderite #37 (Bonderite is a Registered Trade Mark) steel sheets with a wire-wound rod so as to apply a wet film of 0.5 mil thickness. The coated panel was exposed to the predominantly continuum visible light radiation from a 50 kilowatt argon swirl-flow plasma arc at a distance of two feet for a period of five seconds. The cured coating exhibited a Sward hardness of 22 and a reverse impact of 150 inch-pounds.

Example 36

15 A solution of 100 grams of a poly-epsilon-caprolactone triol having an average molecular weight of about 800, 200 ml of benzene and 2 drops of dibutyltin dilaurate was charged to a one-liter resin kettle equipped with motor-driven blade stirrer, reflux condenser, dropping funnel and thermocouple inlet. The poly-epsilon-caprolactone triol was produced by the reaction of epsilon-caprolactone with the adduct of glycerol and 3 moles of ethylene oxide. With stirring and under a slight positive pressure of nitrogen, 88.03 grams of bis(2-isocyanatoethyl) 5-norbornene-2,3-dicarboxylate were added over a period of twenty minutes while maintaining a temperature of 20°C. by means of an external ice bath. Stirring was continued for 4.5 hours at 20°C., 32.3 grams of n-butanol were then added, and the reaction mixture was allowed to stir overnight (16 hours). The temperature was raised to 100°C. and the remaining low boiling components were removed *in vacuo*. The resin was then purged with nitrogen and dumped, yielding 199.5 g of viscous, sticky material. Reduced viscosity of the urethane polymer in benzene (0.5% solution at 30°C.) was 0.086, while in N,N-dimethylformamide (0.5% solution at 30°C.) it was 0.188.

30 Thirty-five grams of the urethane resin described above was mixed with 15 grams neopentyl glycol diacrylate to form a fluid solution. The material was applied as a 1-mil wet film to a Bonderite #37 steel panel. Exposure of the coated panel to the predominantly continuum visible light radiation from a 50 kilowatt argon swirl-flow plasma arc for 20 seconds at a distance of two feet from the arc produced a cured finish. The coating showed an impact resistance greater than 165 pounds per inch, excellent crosshatch adhesion and steam resistance.

Example 37

40 A silicone-modified polyester resin was prepared by reacting 143.9 grams of neopentyl glycol, 84.7 grams of maleic anhydride, 60 grams of xylene, and 214.9 grams of a methoxy-capped linear phenyl- and methyl-substituted siloxane of average mw 450 (214.85 g). The mixture was placed in a one-liter resin kettle equipped with motor-driven blade stirrer, six-inch distillation column, dropping funnel and thermocouple and stirred under reflux, removing a total of 30 ml of methanol and then 24 ml of water over a period of 12 hours. During that time the kettle temperature was raised to a maximum $190 \pm 5^\circ\text{C}$. The siloxane polymer was the reaction product of equimolar amounts of dimethyldichlorosilane diphenyltrichlorosilane and water, capped with methanol. After removal of the water, the still column was replaced with an acetone/dry ice condenser, and 114.2 grams of dicyclopentadiene were added dropwise over a period of three hours at a kettle temperature of 190°C . The temperature was then lowered to $150 \pm 10^\circ\text{C}$., and the excess mono- and/or dicyclopentadiene was removed *in vacuo* with a nitrogen purge. A total of 400.7 g of the silicone-modified polyester resin remained. The material had a reduced viscosity in benzene (0.5% solution at 30°C .) of 0.045. Analysis by infrared and nuclear magnetic resonance spectroscopy indicated that essentially all double bonds were of the norbornene type. Fifteen grams of the silicone-polyester described above were dissolved in a solution of 8.94 g of 2-ethylhexyl acrylate, 1.06 g of neopentyl glycol diacrylate and 0.75 g of benzophenone. A wet film of 0.3 mil thickness was applied to a Bonderite #37 steel panel with a wire-wound rod, and the panel was exposed to the predominantly continuum visible light radiation from a 50 kilowatt argon swirl-flow plasma arc at a distance of two feet. The cured coating exhibited the properties listed below:

		Coating
Exposure		25 sec.
Sward hardness		12
Impact		
	Front	>165
	Reverse	100
Adhesion, crosshatch		Excellent
Boiling water		
	Resistance	Good
	Adhesion	Excellent

Example 38

5 A series of polymers was produced by preparing solutions of 5 grams of the vinyl monomers shown in the following table with various photoinitiators. Each solution was placed in an aluminum cup and irradiated with light from (1) a 550 watt mercury lamp (one foot under the arc) and (2) the continuum light radiation from an argon swirl-flow plasma arc (2 feet under arc). Irradiation was discontinued when the monomer polymerized to the extent that it was no longer fluid, the time needed was recorded as the Exposure Time. 5

Monomer	Additive	Light Source	Exposure Time (sec.)
2-Butoxyethyl acrylate	None	Mercury arc	No polymer after 10 minutes
"	3 wt. % Benzophenone	Mercury arc	200
"	"	Swirl-flow plasma arc	60
"	3% Benzophenone plus 2.0% methyl diethanolamine	Mercury arc	60
"	"	Swirl-flow plasma arc	25
Neopentylglycol diacrylate	None	Mercury arc	No polymer
"	3% Benzophenone	Mercury arc	60
"	3% Benzophenone plus 2.0% methyl diethanolamine	Mercury arc	20
"	"	Swirl-flow plasma arc	3
2-Ethylhexylacrylate	None	Swirl-flow plasma arc	None, Monomer boiled out
"	3% Benzophenone plus 2% methyl diethanolamine	Swirl-flow plasma arc	20
2-Methoxyethyl acrylate	"	Swirl-flow plasma arc	3

Example 39

A padding bath was prepared by dissolving 83.3 grams of 60% aqueous N-methylol-acrylamide (50 g contained), 15 grams of zinc nitrate as catalyst, and 0.5 gram of a surfactant which was the reaction product of a C₁₅ linear secondary alcohol and 9 mols of ethylene oxide in sufficient water to make up a 500 gram solution. Five swatches of 15-inch by 18-inch cotton broadcloth were padded with the solution and passed through a wringer calibrated so that the padded swatches increased 65% by weight by pick-up of the solution. The swatches were then placed on pin frames and exposed to the predominantly continuum visible light radiation from a 50 kilowatt argon swirl-flow plasma arc at a distance of two feet. Exposure times were 1, 3, 5, 10 and 20 seconds. The samples were dried at 200°C. for two minutes in a forced air oven and then cured at 320°C. for five minutes. The degree of durable press imparted by this treatment was measured by the Monsanto Wrinkle Recovery Angle Test (AATCC #66—1959T).

Exposure Time (Seconds)	MWRA (Warp plus fill)
1	223
3	263
5	262
10	270
20	267

The untreated cotton has a MWRA of only 160°

Example 40

One hundred parts of a commercially available polyisochloroprene rubber having an average molecular weight of about 350,000 was blended on a roll mill with 0.3 part of benzophenone and 0.5 part of ethyl eosin. The blend was formed into six inches square plaques having a thickness of 75 mils. The squares were irradiated with the predominantly continuum visible light radiation from a 50 kilowatt argon swirl-flow plasma arc at a distance of two feet from the arc. The extent of crosslinking or cure was determined qualitatively by immersing 9 mm circles cut from the squares in about 110 ml of toluene for a period of 96 hours at room temperature. At the end of this period, the contents of the containers were filtered through a 200 mesh screen and the polymer remaining on the screen was evaluated visually. The unirradiated rubber completely dissolved. The rubber samples that were exposed to the continuum visible light radiation had crosslinked and the extent thereof was dependent on the radiation period. The degree of crosslinking was estimated from the amount of cured rubber remaining on the screen. The circle irradiated for 30 seconds yielded a small amount of a loose, coherent, deformed gel. The circle irradiated for 90 seconds retained its circular shape and exhibited a skin effect, indicative of appreciable crosslinking. The circle irradiated for 120 seconds had a well defined circular form and a strong skin, indicative of a high level of crosslinking.

The process of this invention can also be used to coat wires, such as magnet wire. The coating of wires has long been known, it generally involves the passage of the wire through a coating bath followed by steps to dry the coating on the wire. It is important that the coating be continuous and free of holes. In the instant application, a wire can be coated by passage through an appropriate coating bath containing a crosslinkable polymer, a polymerizable monomer, or mixture thereof, said bath optionally containing fillers, dyes, and other known additives and diluents or solvents. The coated wire is then exposed to the continuum visible light radiation and cured to a solid coating. This process may be repeated as many times as is necessary to obtain the desired coating thickness.

WHAT WE CLAIM IS:—

1. A method for polymerizing a polymerizable ethylenically unsaturated monomer containing at least one polymerizable ethylenically unsaturated group of the structure $>C=C<$ which comprises exposing said monomer to artificial predominantly continuum light radiation from a swirl-flow plasma arc with a radiance of at least 350 watts per square centimeter steradian when integrated throughout the entire spectral range of said continuum light radiation, said predominantly continuum light radiation having at least 70 per cent of the light radiated at a wavelength longer than 4,000 Angstroms and at least some of the light having wavelengths shorter than 4,000 Angstroms.

2. A method as claimed in claim 1, wherein the gaseous medium in the swirl-flow plasma arc means is an inert rare gas.

3. A method for curing a curable organic polymer composition which comprises exposing said polymer to artificial predominantly continuum light radiation from a swirl-flow plasma arc with a radiance of at least 350 watts per square centimeter steradian when integrated throughout the entire spectral range of said continuum light radiation, said predominantly continuum light radiation having at least 70 per cent of the light radiated at a wavelength longer than 4,000 Angstroms and at least some of the light having wavelengths shorter than 4,000 Angstroms.

4. A method as claimed in claim 3, wherein the polymer is an olefin polymer.

5. A method as claimed in claim 4, wherein the polymer is an ethylene polymer.

6. A method as claimed in claim 5, wherein the polymer is polyethylene.

7. A method as claimed in claim 3, wherein the polymer is a siloxane polymer.

8. A method as claimed in claim 3, wherein the polymer is a vinyl polymer.

9. A method as claimed in claim 3, wherein the polymer is an acrylic polymer.

10. A method as claimed in claim 3, wherein the polymer is a urethane polymer.

11. A method as claimed in claim 3, wherein the polymer is a polyester.

12. A method as claimed in claim 3, wherein the polymer is a polyamide.

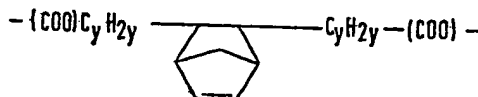
13. A method as claimed in claim 3, wherein the polymer is a norbornenyl polymer.

14. A method as claimed in any one of claims 3 to 13, wherein a crosslinker, photosensitizer or free radical initiator is also present.

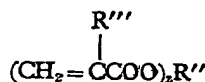
15. A method as claimed in claim 14, wherein the photosensitizer is benzophenone and the free radical initiator is 2,4-dichlorobenzoyl peroxide.

16. A method as claimed in claim 3, wherein the organic polymer composition is a 100 per cent solids coating composition as hereinbefore defined comprising (A) an organic polymer and (B) from 5 to 95 per cent by weight of an acrylyl or vinyl monomer.

17. A method as claimed in claim 16, wherein the organic polymer composition is a 100 per cent solids coating composition comprising (A) a polyester containing in said polyester molecule in polymerized form the norbornenyl group:



wherein y has a value of from 0 to 5 and (B) from 5 to 95 per cent by weight of said composition of an acrylyl compound of the formula:



wherein

R''' is hydrogen or methyl;

z is an integer having a value of from 1 to 4 and is the valence of R'', and R'' is:

a) hydrogen,

b) alkyl of from 1 to 18 carbon atoms,

c) alkoxyalkyl having up to 15 carbon atoms,

d) haloalkyl having up to 15 carbon atoms,

e) cyano,

f) cyanoalkyl wherein the alkyl group has up to 15 carbon atoms,

g) epoxyalkyl wherein the alkyl group has up to 15 carbon atoms,

h) aryl,

i) aryloxyalkyl wherein the alkyl group has up to 15 carbon atoms,

j) trialkoxysiloxyalkyl wherein the alkoxy group has from 1 to 5 carbon atoms and alkyl group has up to 15 carbon atoms,

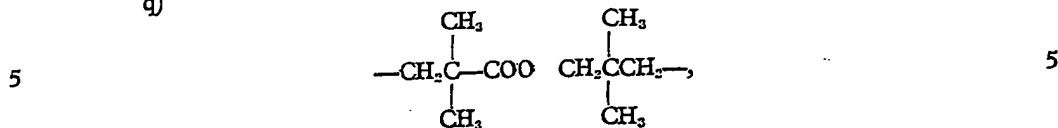
k) $-\text{CONR}_2$ wherein R'' can be hydrogen or hydrocarbyl having up to 15 carbon atoms,

l) dicyclopentenyl,

m) bicyclo[2.2.1]hept-2-en-5-yl,

n) bicyclo[2.2.1]hept-2-en-5-alkyl wherein the alkyl group has from 1 to 4 carbon atoms,

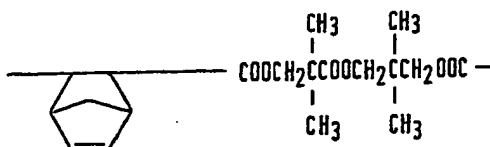
- o) divalent $-C_pH_{2p}-$ wherein p has a value of from 1 to 10,
 p) $-C_wH_{2w}(OC_nH_{2n})_v-$ wherein w has a value of from 2 to 4 and v has a value of from 1 to 5000,
 q)



- r) trivalent C_qH_{2q-1} wherein q has a value of from 3 to 10, and
 s) tetravalent C_sH_{2s-2} wherein s has a value of from 4 to 10.

18. A method as claimed in claim 17, wherein the concentration of the acrylyl compound is from 25 to 55 weight per cent.

19. A method as claimed in claim 17 or claim 18, wherein the polyester has the repeating unit



20. A method as claimed in any one of claims 17 to 19, wherein the polyester has been modified by reaction with an organic isocyanate.

21. A method as claimed in claim 20, wherein the organic isocyanate is bis(2-isocyanatoethyl) 5-norbornene-2,3-dicarboxylate.

22. A method as claimed in any one of claims 16 to 21, wherein a crosslinker, photosensitizer or free radical initiator is also present.

23. A method as claimed in claim 22, wherein the photosensitizer is benzophenone, benzil or 4-methoxybenzophenone.

24. A modification of the method as claimed in any one of claims 16 to 22, wherein R'' may also be a hydroxyalkyl group having up to 10 carbon atoms.

25. A method as claimed in claim 3, wherein the organic polymer is a silicone polymer and a crosslinker, photosensitizer or free radical initiator is also present.

26. A method for producing an electrical conductor, which method comprises extruding an ethylene polymer on the metal conductor and curing said polymer by a method as claimed in claim 3.

27. A method as claimed in claim 26, wherein the polymer is polyethylene.

28. A method for producing a treated fabric which method comprises the steps of treating said fabric with at least one polymerizable ethylenically unsaturated monomer and then exposing said treated fabric to artificial predominantly continuum light radiation from a swirl-flow plasma arc with a radiance of at least 350 watts per square centimeter steradian when integrated throughout the entire spectral range of said continuum light radiation, said predominantly continuum light radiation having at least 70 per cent of the light radiated at a wavelength longer than 4,000 Angstroms and at least some of the light having wavelengths shorter than 4,000 Angstroms.

29. A method as claimed in claim 1 substantially as hereinbefore described with reference to Example 38 or 39.

30. An olefin polymer whenever produced by a method as claimed in claim 1, 2 or 29.

31. A method as claimed in claim 3 substantially as hereinbefore described with reference to any one of Examples 1 to 34.

32. An organic polymer composition whenever cured by a method as claimed in any one of claims 3 to 23 and 31.

33. A method as claimed in claim 3 substantially as hereinbefore described with reference to any one of Examples 35, 36, 37 and 40.

34. An organic polymer composition whenever cured by a method as claimed in claim 33.

35. A method as claimed in claim 26 substantially as hereinbefore with reference to Example 31.

36. An electrical conductor whenever produced by a method as claimed in claim 26, 27 or 35.

37. A method as claimed in claim 28 substantially as hereinbefore described in Example 32.

38. A fabric whenever produced by a method as claimed in claim 28.

39. A method as claimed in claim 28 substantially as hereinbefore described in Example 39.

40. A fabric whenever produced by a method as claimed in claim 37.

41. A fabric whenever produced by a method as claimed in claim 39.

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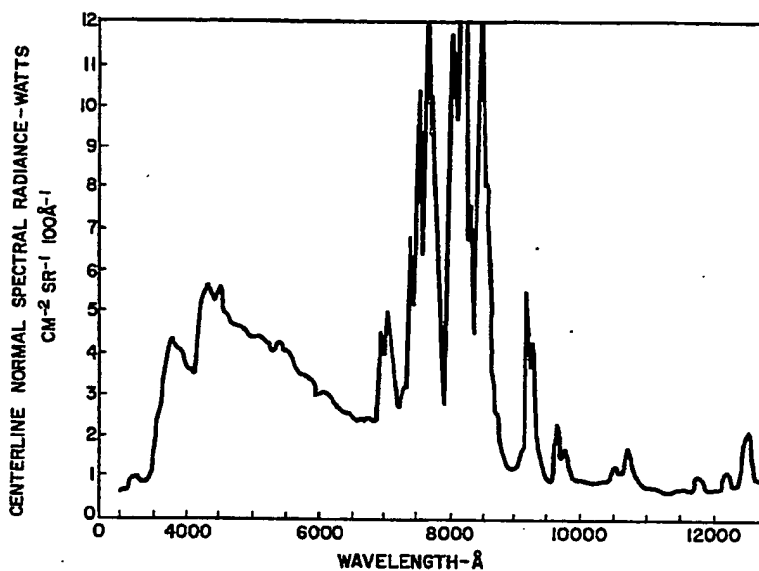


FIG. 1.

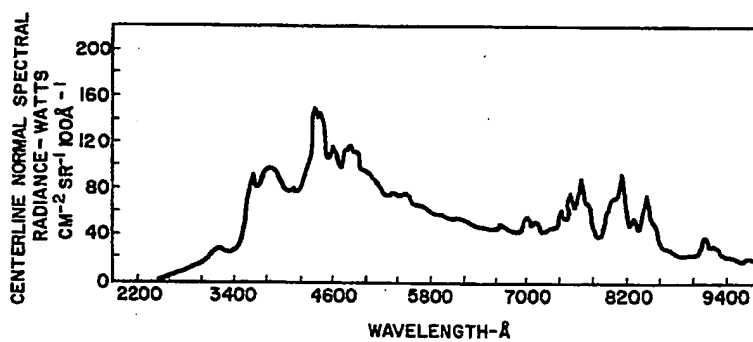


FIG. 3.

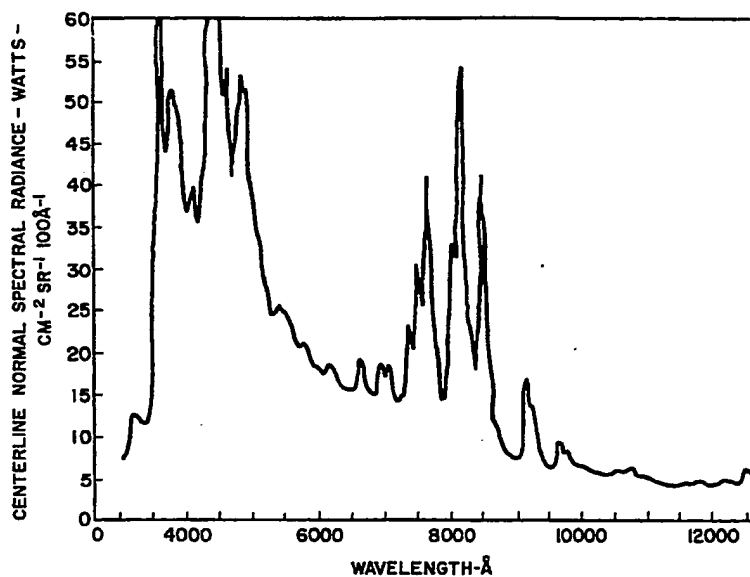


FIG. 2.

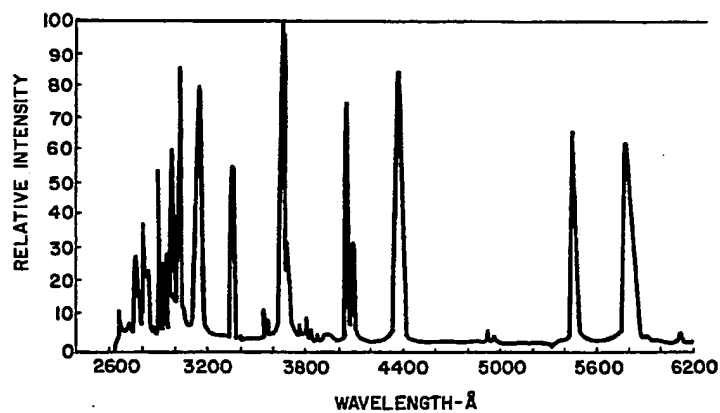


FIG. 4.